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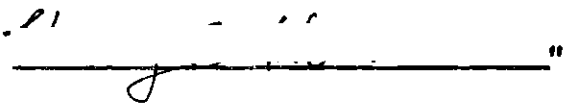

DISPROPORTIONATION AND ISOMERIZATION REACTIONS OF CERTAIN ALKYL- AND HALOBENZENES

A THESIS

Presented to

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by

Henry Earl Harris

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DISPROPORTIONATION AND ISOMERIZATION

REACTIONS OF CERTAIN ALKYL- AND HALOBENZENES

Approved:

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SUMMARY

As one of the first of the major steps toward making organic chemistry a quantitative science, Hammett found that a large amount of rate and equilibrium data of meta- and para-substituted compounds could be correlated using the equation

$$\log \frac{K_y^x}{K_o^x} = \rho_x \sigma_y$$

where the terms K_o^x and K_y^x refer to the data on the unsubstituted and meta- or para-substituted compounds respectively, sigma is known as the substituent constant and rho as the reaction constant. Each substituent, Y, was given a meta sigma and also a para sigma value. The value of a reaction constant depended only upon the reaction (under a given set of conditions) but not upon the orientation of the substituent.

Hine has shown that the reaction constant for an equilibrium process is proportional to the difference in the substituent constants for the two groups being equilibrated. This derivation was made algebraically assuming the applicability of the Hammett equation or a more general Hammett-type equation in which the reaction constants for meta- and para-substituted compounds need not be identical. The constant of proportionality is called tau. Thus for the equilibria of two related compounds

$$\underline{m}\text{-}X_1C_6H_4Y_1 \xrightleftharpoons{K^{y}_{m\text{-}x_1}} \underline{m}\text{-}X_1C_6H_4Y_2$$

$$\underline{m}\text{-}X_2C_6H_4Y_1 \xrightleftharpoons{K^{y}_{m\text{-}x_2}} \underline{m}\text{-}X_2C_6H_4Y_2$$

Application of the Hammett equation yields

$$\log \frac{K^{y}_{\underline{m}\text{-}x_1}}{K^{y}_{\underline{m}\text{-}x_2}} = \rho_y(\sigma_{\underline{m}\text{-}x_1} - \sigma_{\underline{m}\text{-}x_2})$$

and applying the relation

$$\rho_y = \tau_{\underline{m}}(\sigma_{\underline{m}\text{-}y_1} - \sigma_{\underline{m}\text{-}y_2})$$

derived by Hine, yields

$$\log \frac{K^{y}_{\underline{m}\text{-}x_1}}{K^{y}_{\underline{m}\text{-}x_2}} = \tau_{\underline{m}}(\sigma_{\underline{m}\text{-}y_1} - \sigma_{\underline{m}\text{-}y_2})(\sigma_{\underline{m}\text{-}x_1} - \sigma_{\underline{m}\text{-}x_2})$$

A similar equation could also be derived for <u>para</u>-substituted compounds, but would require resonance terms to apply in cases in which direct interaction between the reaction center and the substituent is possible.

Application of the above equation to the reaction

$$C_6H_5X + C_6H_5Y \rightleftharpoons C_6H_6 + \underline{m}\text{-}XC_6H_4Y$$

yields the relation

$$\log 3K_d(\underline{\text{meta}}) = -\tau_{\underline{m}}\sigma_{\underline{m}\text{-}x}\sigma_{\underline{m}\text{-}y}$$

where $K_d(\underline{\text{meta}})$ is equal to the ratio $[C_6H_6][\underline{m}\text{-}XC_6H_4Y]/[C_6H_5X][C_6H_5Y]$,

tau applies to the conditions used and "3" is a statistical correction. Similarly the equation

$$\log {}^{6}K_{d}(\underline{para}) = -\tau_{\underline{p}}\sigma_{\underline{p}\text{-}X}\sigma_{\underline{p}\text{-}y}$$

may be derived for the reaction

$$C_6H_5X + C_6H_5Y \rightleftharpoons C_6H_6 + \underline{p}\text{-}XC_6H_4Y$$

The purpose of the present research was to obtain equilibrium data applicable to the equations derived here and thus test these relations. Deviations from the Hammett equation are most commonly attributed to four factors: resonance interactions between substituent groups, solvation, hydrogen bonding and complications peculiar to rate processes, such as changes in reaction mechanisms. Thus reactions were chosen to minimize these complications.

The disproportionation of bromobenzene into benzene and dibromobenzenes

$$C_6H_5Br + C_6H_5Br \rightleftharpoons C_6H_6 + \underline{o}\text{-}, \underline{m}\text{-} \& \underline{p}\text{-}BrC_6H_4Br$$

catalyzed by aluminum bromide-hydrogen bromide was studied. It was shown that the catalyst concentration (in low concentration ranges, at least) did not significantly alter the equilibrium constants. The equilibrium constants were approached from both high and low values with essentially the same values being obtained. The effect of temperature on the equilibrium constants was also studied. All of the analyses were carried out using gas-liquid chromatography.

Several other reactions were studied at 35.0°. In each case the

equilibrium constants were approached from higher and lower values. In the reaction of bromobenzene with fluorobenzene to yield the bromofluorobenzenes the analysis was carried out using gas-liquid chromatography. The concentrations of benzene, bromobenzene, toluene and the bromotoluene isomers in the reaction of bromobenzene with toluene were determined using a combination of gas-liquid chromatography and infrared spectroscopy. Attempts to bring about the reaction of bromobenzene with anisole or diphenyl ether resulted in cleavage of the ether linkage.

A number of attempts were made to obtain equilibrium constants for the disproportionation of toluene without success. Ethylbenzene was found to undergo disproportionation readily at 35.0° and the equilibrium constants were determined using gas-liquid chromatography. Data on ethylbenzene were used as a substitute for that on toluene.

Using the equations applicable to the equilibrium constants, tau values were calculated using Hammett sigma values based on the ionization of benzoic acids. The inconsistency of the resulting values showed that the Hammett constants could not correlate the data.

Values of τ_m and τ_p equal to 3.5 were found by Hine to apply to aqueous solution. Haworth found that the value of tau has little dependence on the solvent. Therefore, using 3.5 for the tau values, sigma values were calculated for the substituents involved. However, the sigma values calculated for the ethyl group using the disproportionation constants of ethylbenzene were quite different from those calculated for the methyl group using the data from the reaction of bromobenzene with toluene.

Thus it was concluded that neither the Hammett equation nor even the more general dual-rho equation is applicable to equilibria of the type studied in this research.

CHAPTER I

INTRODUCTION

Hammett found that a large number of rate and equilibrium data on reactions of *meta*- and *para*-substituted benzene derivatives fit the equation

$$\log \frac{K}{K_o} = \rho \log \frac{K'}{K'_o} \qquad (1\text{-}1)$$

K and K_o refer to the data on the substituted and unsubstituted compounds respectively. Because of the large number of accurate data available, the ionization of benzoic acids in aqueous solution at 25° was chosen as the standard reaction, and a new constant, *sigma*, was defined as $\log (K'/K'_o)$, where K'_o and K' are the ionization constants of benzoic acid and the substituted acid, respectively. This definition reduced equation (1-1) to the Hammett equation (1,2)

$$\log \frac{K}{K_o} = \rho\sigma \qquad (1\text{-}2)$$

where *sigma* is known as the substituent constant and *rho* as the reaction constant. Each substituent was given a *meta* and also a *para sigma* value. However, each reaction, under a given set of conditions, was given only one *rho* value to be used with both *meta*- and *para*-substituted compounds,

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1. L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 184; *Chem. Revs.*, *17*, 125 (1935); *J. Am. Chem. Soc.*, *59*, 96 (1937).

2. H. H. Jaffe, *Chem. Revs.*, *53*, 191 (1953).

Large deviations from the Hammett equation occur in cases in which direct resonance interaction between the substituent and the reaction center is possible. This fact has led to the use of σ^- (sigma minus) values (1,2,3) and σ^+ (sigma plus) values (4). However, van Bekkum, Verkade and Wepster (5) have presented evidence that a continuous range of sigma values would be required to correlate existing data in cases where there seems to be direct resonance interaction between substituent and reaction center.

Hine (6) has shown that the reaction constant for an equilibrium process is proportional to the difference in the substituent constants for the two groups being equilibrated. This derivation was made algebraically, assuming the applicability of the Hammett equation or a more general Hammett-type equation in which the reaction constants for meta- and para-substituted compounds need not be identical. The constant of proportionality is called tau. Thus, for the equilibria for two related compounds

$$m\text{-}X_1C_6H_4Y_1 \underset{}{\overset{K^y_{m\text{-}X_1}}{\rightleftharpoons}} m\text{-}X_1C_6H_4Y_2 \qquad (1\text{-}3)$$

$$m\text{-}X_2C_6H_4Y_1 \underset{}{\overset{K^y_{m\text{-}X_2}}{\rightleftharpoons}} m\text{-}X_2C_6H_4Y_2 \qquad (1\text{-}4)$$

application of the Hammett equation yields

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3. R. W. Taft, Jr., J. Am. Chem. Soc., 79, 1045 (1957).

4. H. C. Brown and Y. Okamoto, ibid., 80, 4979 (1958).

5. H. van Bekkum, P. E. Verkade and B. M. Wepster, Rec. trav. chim., 78, 815 (1959).

6. J. Hine, J. Am. Chem. Soc., 81, 1126 (1959).

$$\log \frac{K^{y}_{m\text{-}x_1}}{K^{y}_{m\text{-}x_2}} = \rho^{m}_{y}(\sigma_{x_1} - \sigma_{x_2})$$

and applying the relation

$$\rho^{m}_{y} = \gamma_{m}(\sigma_{m\text{-}y_1} - \sigma_{m\text{-}y_2})$$

derived by Hine, yields

$$\log \frac{K^{y}_{m\text{-}x_1}}{K^{y}_{m\text{-}x_2}} = \gamma_{m}(\sigma_{m\text{-}y_1} - \sigma_{m\text{-}y_2})(\sigma_{m\text{-}x_1} - \sigma_{m\text{-}x_2}) \qquad (1\text{-}5)$$

This equation may also be derived from free energy considerations (7). Assume that from the total energy of a molecule there may be separated a part to be called the free energy of polar interaction, whose magnitude may be calculated from certain properties of the substituent groups called their polar substituent constants. Thus, for $m\text{-}X_1C_6H_4Y_1$ the free energy of polar interaction of the substituent groups is assumed to be represented by the equation

$$F^{m\text{-}X_1C_6H_4Y_1}_{p.i.} = 2.3RT\,\gamma_{m}\sigma_{m\text{-}x_1}\sigma_{m\text{-}x_2}$$

where the σ_{m}'s are polar substituent constants characteristic of the interaction of the substituents with other substituents meta to them, γ_{m} is a proportionality constant describing the efficiency of such meta interactions in the solvent at the temperature under consideration, and the 2.3 RT has been inserted for convenience. Thus the free energy change for the reactions (1-3) and 1-4) will be given by

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7. J. Hine, ibid., 82, 4877 (1960).

$$\Delta F = 2.3RT \log \frac{K^{y}_{\underline{m}\text{-}X_1}}{K^{y}_{\underline{m}\text{-}X_2}}$$

$$\Delta F = F^{\underline{m}\text{-}X_1C_6H_4Y_1}_{p.i.} + F^{\underline{m}\text{-}X_2C_6H_4Y_2}_{p.i.} - F^{\underline{m}\text{-}X_1C_6H_4Y_2}_{p.i.} - F^{\underline{m}\text{-}X_2C_6H_4Y_1}_{p.i.}$$

$$\Delta F = 2.3RT\, \rho_{\underline{m}}(\sigma_{\underline{m}\text{-}Y_1} - \sigma_{\underline{m}\text{-}Y_2})(\sigma_{\underline{m}\text{-}X_1} - \sigma_{\underline{m}\text{-}X_2})$$

which leads to equation (1-5) or in the case of the unsubstituted compound (X_2 = H), to the form

$$\log \frac{K^{y}_{\underline{m}\text{-}X_1}}{K^{y}_{o}} = \rho_{\underline{m}}\sigma_{\underline{m}\text{-}X_1}(\sigma_{\underline{m}\text{-}Y_1} - \sigma_{\underline{m}\text{-}Y_2}) \qquad (1\text{-}6)$$

since hydrogen's <u>sigmas</u> are defined as zero. Such an equation also could be derived for <u>para</u>-substituted compounds, but would require resonance terms (7) to apply in cases in which direct interaction between the reaction center and the substituent is possible. The relation

$$-\log 3K_d(\underline{meta}) = \rho_{\underline{m}}\sigma_{\underline{m}\text{-}X}\sigma_{\underline{m}\text{-}Y}$$

is derived using equation (1-6) for the reaction

$$C_6H_5X + C_6H_5Y \rightleftharpoons C_6H_6 + \underline{m}\text{-}XC_6H_4Y$$

and for the reaction

$$C_6H_5X + C_6H_5Y \rightleftharpoons C_6H_6 + \underline{p}\text{-}XC_6H_4Y$$

$$\log 6K_d(\underline{para}) = -\rho_{\underline{p}}\sigma_{\underline{p}\text{-}X}\sigma_{\underline{p}\text{-}Y}$$

where

$$K_d = [C_6H_6][\underline{m}\text{- or } \underline{p}\text{-}XC_6H_4Y]/[C_6H_5X][C_6H_5Y]$$

"3" and "6" are statistical corrections (8) made necessary by the larger number of modes of reaction available for the reverse reactions, and the tau's refer to the reaction conditions used.

Deviations from the Hammett equation are most commonly attributed to four factors: resonance interactions between substituent groups and reaction centers, solvation of electrically charged groups, hydrogen bonding and complications peculiar to rate processes, such as changes in reaction mechanisms. These factors should be minimized in obtaining data to apply to the equations that have been discussed. The purpose of the research reported here was to obtain equilibrium data on reactions of the types discussed here. Several such reactions have been reported in the literature.

Bromobenzene has been found to disproportionate to benzene and dibromobenzene readily in the presence of aluminum bromide at room temperature but the reaction has only received a preliminary study (9). A disproportionation constant,

$$K_d = [C_6H_6][C_6H_4Br_2]/[C_6H_5Br]^2$$

at 25°, of approximately 0.04, with the p-dibromobenzene as the major isomer, was reported. Catalyst concentrations as low as 2 mole per cent were used.

Reactions of aromatic hydrocarbons in the presence of Friedel-Crafts type catalysts are complicated by the formation of highly colored

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8. S. W. Benson, ibid., 80, 5151 (1958).

9. F. Fairbrother and N. Scott, Chem. & Ind. (London), 998 (1953).

hydrocarbon-insoluble oils. Brown and Wallace (10), who have made a study of the oils formed when hydrogen bromide is bubbled into a solution of aluminum bromide in aromatic hydrocarbons, report that the oil is a complex consisting of a protonated aromatic ring, $ArH_2^{\oplus}$, and the anion, $Al_2Br_7^{\ominus}$, accompanied by some aromatic hydrocarbon of solvation and thus possesses the formula $(ArH)_x \cdot HBr \cdot Al_2Br_6$. For toluene x is equal to 6.28. For various aromatic hydrocarbons the stability of the complexes decreases in the order: mesitylene $\rangle$ m-xylene $\rangle$ toluene $\rangle$ benzene. The m-xylene complex is more stable than that of o- or p-xylene. Equilibrium data reported in the literature are often misleading because the sampling technique has included taking samples of the oil layer, which contains complexed hydrocarbons.

The disproportionation of toluene to benzene and the xylenes was reported by Pitzer and Scott (11) using 5 mole per cent each of aluminum bromide (as Al_2Br_6) and hydrogen bromide at 50°. The results are shown in Table I. The xylenes produced were of equilibrium composition at the end of both experiments. The analysis for benzene, toluene and the xylene fraction was done by fractional distillation and the xylene distribution was determined using refractive index measurements and therefore the accuracy of the results is probably low. The disproportionation of toluene has also been reported recently by Schriesheim (12)

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10. H. C. Brown and W. J. Wallace, J. Am. Chem. Soc., 75, 6264, 6268 (1953).

11. K. S. Pitzer and D. W. Scott, ibid., 65, 803 (1943).

12. A. Schriesheim, J. Org. Chem., 26, 35 (1961).

Table 1

Constants Calculated for the

Disproportionation of Toluene from Various Data[a]

Temperature	K_d(meta)	K_d(para)	Meta/para	Ortho/para
50.0°	0.12[b]	0.03	4.2	0.7
50.0°	0.18[c]	0.04	4.2	0.7
80.6°	0.79[d]	--	--	--
50.0°	0.20 ± 0.04[e]	0.076 ± 0.008	2.6	0.9
27.0°	0.21[f]	0.08	2.5	0.7
100.0°	0.21[f]	0.09	2.3	0.8
50.0°	--	--	2.9[g]	0.86

[a]No solvent was used other than the aromatic hydrocarbons involved.

[b]From Pitzer and Scott (11), starting with toluene and benzene.

[c]From (11), starting with benzene, toluene and (excess) xylene.

[d]From Schriesheim (12), starting with toluene; the xylene fraction was essentially all meta isomer.

[e]From Taylor, et al., (13); the concentrations calculated from thermodynamic data.

[f]From Hastings and Nicholson (14); the concentrations calculated from thermodynamic data.

[g]From Allen and Yats (15) on the isomerization of the xylenes in toluene.

using 25 mole per cent each of aluminum bromide and hydrogen bromide at 80.6°. The results are given in Table I. The xylene fraction was essentially all meta isomer at 80.6°. The results reported are of little value as equilibrium data since the catalyst concentration used was so large and the complexed hydrocarbons were included in the samples taken.

Concentrations of benzene, toluene, and the xylenes expected from the disproportionation of toluene at 50° have been calculated from thermodynamic data (13). Some constants calculated from these data are given in Table I. This work has recently been slightly modified and extended to include equilibria among benzene and all the methylbenzenes (14).

Allen and Yats (15) studied the isomerization of dilute solutions of the xylenes (0.8 mole) in toluene (7.2 mole) using aluminum chloride (0.2 mole) and hydrogen chloride at 50°. Apparently no disproportionation of the toluene was observed. An equilibrium xylene distribution of 18 per cent ortho, 61 per cent meta and 21 per cent para was reported.

The isomerization of dilute solutions of the ethyltoluenes in toluene was studied (16) at room temperature. A distribution of 9.0

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13. W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer and F. D. Rossini, J. Research Natl. Bur. Standards, 37, 95 (1946).

14. S. H. Hastings and D. E. Nicholson, J. Chem. Eng. Data, 6, 1 (1961).

15. R. H. Allen and L. D. Yats, J. Am. Chem. Soc., 81, 5289 (1959).

16. R. H. Allen, L. D. Yats and D. S. Erley, ibid., 82, 4853 (1960).

per cent o-, 65.0 per cent m- and 26.0 per cent p-ethyltoluene was reported.

The disproportionation of ethylbenzene catalyzed by aluminum bromide-hydrogen bromide is much faster than that of toluene (17,18) and although many workers have studied this reaction there appeared to be no equilibrium data that could be used. Lien and McCaulay (19) reported values for K_d of 0.20 to 0.28 with the diethylbenzene fractions consisting of 60 to 75 per cent of the meta isomer.

The isomerization of the dichlorobenzenes has been studied (20, 21) using aluminum chloride. Temperatures of 120° to 180° were used but the reaction was very slow at 120°. Only about 1.6 per cent chlorobenzene was formed by the disproportionation of the dichlorobenzenes at 160° for 50 hours.

Although Fairbrother and Scott (9) introduced no hydrogen bromide into the solution of bromobenzene and aluminum bromide, they presented evidence that hydrogen bromide, probably produced by hydrolysis of aluminum bromide by traces of moisture present in the system, is an essential co-catalyst in the disproportionation. The hydrogen bromide-aluminum bromide couple, which possesses very high proton-transfer capabilities (10), attacks the aromatic ring forming a sigma complex (I).

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17. G. Baddeley, G. Holt and D. Voss, J. Chem. Soc., 100 (1952).

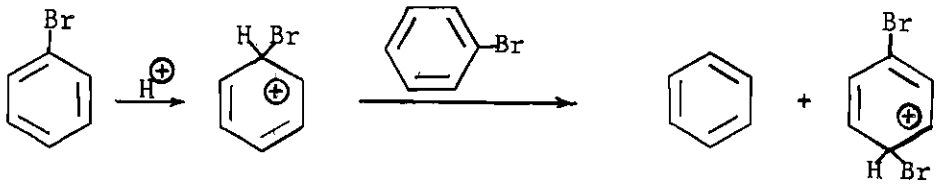
18. H. C. Brown and C. R. Smoot, J. Am. Chem. Soc., 78, 2176 (1956).

19. A. P. Lien and D. A. McCaulay, ibid., 75, 2407 (1953).

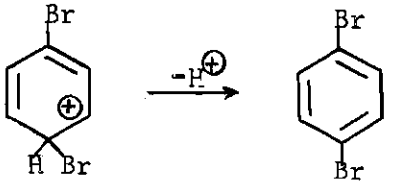
20. A. A. Spryskov and Yu. G. Erykalov, J. Gen. Chem. U. S. S. R. (Eng. Tran.), 28, 1668 (1958).

21. A. A. Spryskov and Yu. G. Erykalov, ibid., 29, 2798 (1959).

The sigma complex may react either by a direct displacement of its activated bromine atom by a molecule of bromobenzene



(I)



or by dissociation to benzene and a bromine cation, $Br^{\oplus}$, which brominates a molecule or bromobenzene.

Baddeley, Holt and Voss (17) showed that hydrogen bromide is also essential to the aluminum bromide-catalyzed isomerization of the xylenes or disproportionation of ethylbenzene.

The disproportionation of aromatic hydrocarbons such as toluene or ethylbenzene has been considered (18, 22) to proceed by formation of a sigma complex followed by a displacement of the alkyl group by a molecule of alkylbenzene to give benzene and the dialkylbenzene. However, Streitwieser and co-workers (23, 24) have presented evidence that the

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22. D. A. McCaulay and A. P. Lien, J. Am. Chem. Soc., 75, 2411 (1953).

23. A. Streitweiser, Jr. and L. Reif, ibid., 82, 5003 (1960).

24. A. Streitweiser, Jr. and W. J. Downs, J. Org. Chem., 27, 625 (1962).

disproportionation of ethylbenzene proceeds through intermediate formation of 1-(ethylphenyl)-1-phenylethanes, which react under the influence of aluminum bromide and hydrogen bromide to give benzene and diethylbenzenes.

The isomerization of disubstituted benzene derivatives may proceed by either an intramolecular or an intermolecular mechanism. If the intramolecular route is followed the group moves in a 1,2-shift from one carbon to an adjacent one. In the intermolecular mechanism the group shifts between aromatic rings, the group from a disubstituted ring either attacking a monosubstituted ring to give the isomerized disubstituted derivative directly, as in reaction (1-7), or attacking benzene, if present, in a reversal of the disproportionation reaction (1-8).

$$\underline{o}\text{- \& } \underline{p}\text{-}C_6H_4XY + C_6H_5Y^* \rightleftharpoons C_6H_5Y + \underline{m}\text{-}XC_6H_4Y^* \qquad (1\text{-}7)$$

$$C_6H_5X + C_6H_5Y \rightleftharpoons C_6H_6 + \underline{o}\text{-, } \underline{m}\text{- \& } \underline{p}\text{-}XC_6H_4Y \qquad (1\text{-}8)$$

Isomerization of a <u>para</u> isomer by the intramolecular mechanism would proceed <u>via</u> the intermediate formation of the <u>meta</u> isomer. McCaulay and Lien (25) proved that the isomerization of the xylenes proceed by this mechanism by showing that the <u>meta</u> isomer was the initially formed product in the isomerization of both <u>p</u>- and <u>o</u>-xylene, as in reaction (1-9).

In intermolecular reactions of the types discussed, the migrating group loses its bonding electrons to the ring that it leaves and gains

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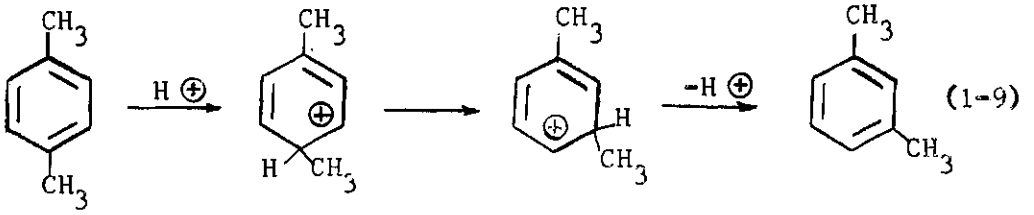
25. D. A. McCaulay and A. P. Lien, <u>J. Am. Chem. Soc.</u>, <u>74</u>, 6246 (1952).



(1-9)

a new pair from the new ring. Therefore, the new ring is subjected to an electrophilic attack and the initial products should be the kinetically controlled ones. For example, a chlorination of chlorobenzene (26) yields an isomer distribution of 88 per cent p-, 11 per cent o- but only 1 per cent m-dichlorobenzene; that is, the chloro group is an ortho-para director and the kinetically controlled product contains very little meta isomer. Disproportionation, which, of course, proceeds by an intermolecular mechanism would be expected to accompany intermolecular isomerization. Spryskov and Erykalov (20, 21) proposed that the isomerization of the dichlorobenzenes proceeds by an intermolecular mechanism but this is not consistent with their observations that very little disproportionation accompanied the isomerization and that the isomerization of both o- and p-dichlorobenzene proceed with an initial build-up of the meta isomer.

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26. P. Kovacic and N. O. Brace, ibid., 76, 5491 (1954).

CHAPTER II

EXPERIMENTAL RESULTS

Chemicals[1]

Aluminum Chloride.--Baker Analyzed reagent grade aluminum chloride was used without purification. It was assumed that this was not necessary as no residue was left by vacuum-sublimation of one sample.

Anisole.--Stock anisole was distilled using column No. 1. Gas-liquid chromatography[2] analysis using column C at 125° and 25 p.s.i. showed that less than 0.2 per cent impurities, including phenol, was present.

Benzene.--Matheson, Coleman and Bell industrial grade thiophene-free benzene was distilled using column No. 1. The benzene was analyzed using several g.l.c. columns and no impurities amounting to greater than 0.05 mole per cent were detected.

Bromine.--Baker Analyzed reagent grade bromine was used.

Bromobenzene.--Bromobenzene prepared by undergraduate students was distilled twice using column No. 3.

Eastman white label bromobenzene was distilled through column No. 1. The maximum impurity content was found to be 0.02 mole per cent using several g.l.c. columns.

m-Bromofluorobenzene.--Pierce Chemical Company m-bromofluorobenzene was distilled using column No. 2. G.l.c. analysis using column P, which

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[1]The boiling and melting points that were determined are listed in Tables 2, 3, and 4 at the end of this section.

[2]In following discussions the abbreviation g.l.c. will be used.

gives excellent separation of the meta and para isomers, showed less than 0.05 per cent impurities present. Analysis on Golay column Q at 103° confirmed these results.

p-Bromofluorobenzene.--Eastman white label p-bromofluorobenzene was distilled using column No. 2. Analysis was carried out using column P and the Golay column Q. An impurity of 1.6 per cent of the ortho isomer was found.

o-Bromofluorobenzene.--Pierce Chemical Company o-bromofluorobenzene was distilled through column No. 2. An impurity of 0.36 per cent of the para isomer was detected using column P and the Golay column Q.

m-Bromotoluene.--Eastman white label m-bromotoluene was distilled through column No. 1. By g.l.c. analysis using the Golay column Q an impurity of 0.5 per cent ortho isomer was found. No available g.l.c. column would effect the separation of the meta and para isomers. An upper limit of 2.1 per cent para isomer was set by infrared analysis at 12.445 microns.[3]

p-Bromotoluene.--Eastman white label p-bromotoluene was distilled using column No. 1 and recrystallized from methanol. The product was analyzed by the g.l.c. method as described for the meta isomer. A trace of the ortho isomer, less than 0.05 per cent, was detected. An upper limit of 2.3 per cent meta isomer was set by infrared analysis at 12.966 microns.[3] Repeated recrystallization had no effect on the meta content as determined by the infrared analysis.

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[3]Details are given in the Appendix.

o-Bromotoluene.--Eastman white label o-bromotoluene was distilled using column No. 1. G.l.c. analyses as described for the meta isomer showed no impurities in concentration greater than about 0.02 mole per cent.

Chlorobenzene.--Stock chlorobenzene was distilled using column No. 1.

m-Dibromobenzene.--Eastman white label m-dibromobenzene was distilled under water-aspirator vacuum using a three-foot spinning-band column. Analysis was carried out using the Golay column R at 125° and 30 p.s.i. A small amount of bromobenzene, less than 0.08 mole per cent, was present. No other dibromobenzene isomer was detected. However, the lowest detectable concentration of the para isomer was found to be about one per cent. The para isomer was hard to detect in this case because it was the second of the two not-completely-separable isomers eluted from the column.

The maximum concentration of the para isomer in the m-dibromobenzene was found to be 0.34 per cent by infrared analysis at 12.310 microns.

p-Dibromobenzene.--Eastman white label p-dibromobenzene was recrystallized from methanol. No other isomer was detected using the g.l.c. method described for the meta isomer and since the meta isomer is eluted first, its presence is easily detectable at concentrations around 0.05 mole per cent.

o-Dibromobenzene.--Eastman white label o-dibromobenzene was analyzed by the g.l.c. method described for the meta isomer. Bromobenzene and p-dibromobenzene were found to be present in concentrations of approximately 0.8 and 0.1 mole per cent respectively. Since such small amounts of the o-dibromobenzene were used in the standards and since a knowledge of

the ortho concentration of the samples was not essential to the calculation of the disproportionation constants no further purification or corrections were carried out.

m-Dichlorobenzene.--Eastman white label m-dichlorobenzene was used without purification.

p-Dichlorobenzene.--Matheson, Coleman and Bell p-dichlorobenzene was recrystallized from methanol.

o-Dichlorobenzene.--Eastman practical grade o-dichlorobenzene was distilled using column No. 2. G.l.c. analysis showed the presence of about 8.0 per cent of the para isomer.

Diethylbenzene.--Eastman technical grade diethylbenzene was distilled over sodium through column No. 1. G.l.c. analysis using column Q gave a meta/para value of 1.18.

m-Diethylbenzene.--Two different samples of m-diethylbenzene were used. As a standard, American Petroleum Institute standard sample, mole per cent impurity, 0.07 $\pm$ 0.04, was used. As a reactant Aldrich Chemical Company m-diethylbenzene distilled over sodium was used. G.l.c. analysis using the Golay column Q showed that less than 0.5 per cent impurities was present.

p-Diethylbenzene.--The sources and purities of the p-diethylbenzene samples were the same as for the meta isomer.

o-Diethylbenzene.--American Petroleum Institute standard o-diethylbenzene was used.

Diphenyl Ether.--Distilled diphenyl ether was obtained from Dr. Dewey Carpenter.

Ethylbenzene.--Eastman white label ethylbenzene was distilled through column No. 1. Analysis on the Golay column Q at 100° and 30 p.s.i showed no impurities in concentrations greater than about 0.05 per cent.

Fluorobenzene.--Matheson, Coleman and Bell fluorobenzene was distilled using column No. 2. G.l.c. analysis on column P showed that no impurities, including benzene, were present in concentration greater than about 0.02 per cent.

Hydrogen Bromide.--Matheson anhydrous hydrogen bromide was used as obtained from the cylinder.

Isooctane.--Matheson, Coleman and Bell industrial grade 2,2,4-trimethylpentane was distilled over sodium using column No. 1.

Phenol.--National Aniline C. P. grade phenol was used.

1,2,4,5-Tetrabromobenzene.--Eastman white label product was used.

Toluene.--Baker Analyzed reagent grade toluene was distilled using column No. 1. Analysis by g.l.c. column P showed the only impurity to be about 0.07 mole per cent benzene.

1,3,5-Tribromobenzene.--Eastman white label product was used.

Xylenes.--Eastman white label products were distilled over sodium using column No. 4.

Synthesis of Aluminum Bromide (27).--To a 200 ml. three-neck flask fitted with an air-cooled condenser and a dropping funnel containing

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27. D. G. Nicholson, P. K. Winter and H. Fineberg, Inorganic Synthesis, Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 33.

34 ml. (0.65 mole) of bromine, was added 40.6 g. (1.5 mole) of aluminum pellets. The flask was kept under a slight positive pressure of nitrogen by means of a bubbler connected through the condenser. The aluminum was heated with a flame and bromine was added cautiously. The dropwise addition of bromine was continued at a rate sufficient to keep the reaction going without additional heating.

After the addition of about 1/3 of the bromine the reaction became hard to control. Aluminum bromide began to solidify on the bromine delivery tube stopping the flow of bromine. When the reaction vessel was heated, causing the aluminum bromide to melt, the trapped bromine ran into the flask causing a vigorous reaction. Additional bromine vaporized due to the heat of the reaction and remained in the vapor phase.

The addition of bromine was stopped and the reaction mixture was refluxed over the aluminum to complete the reaction. The resulting aluminum bromide was a clear liquid and solidified to a colorless crystalline solid.

Aluminum bromide was distilled under nitrogen into a receiver to which four glass ampoules were connected. The ampoules were sealed under water-aspirator vacuum and removed from the receiver. The process was repeated by attaching more ampoules to the receiver and distilling more aluminum bromide.

Synthesis of 1,2,4-Tribromobenzene.--By the method of Jackson and Gallivan (28), 30 g. (0.223 mole) of acetanilide (Fischer, U.S.P.) was

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28. C. L. Jackson and F. B. Gallivan, Am. Chem. J., 18, 238 (1896).

converted into 50 g. (0.20 mole) 2,4-dibromoacetanilide, 20 g. (0.08 mole) of which was converted into 7 g. (0.02 mole) of 1,2,4-tribromobenzene. The product was twice recrystallized from absolute ethanol.

Synthesis of 1,2,3-Tribromobenzene.--Twenty-two grams (0.088 mole) of 2,6-dibromoaniline were prepared from 65 g. (0.311 mole) of sulfanilic acid (stock, recrystallized from water) by the procedure of Orton and Pearson (29). This was converted to 1,2,3-tribromobenzene by a Sandmeyer reaction (30). A suspension of 18.2 g. (0.0726 mole) of 2,6-dibromoaniline in 50 ml. of 48 per cent hydrobromic acid was cooled to 5°. A solution of 5.2 g. (0.075 mole) of sodium nitrite in 10 ml. of water was added dropwise. In a three-neck flask fitted with a steam inlet, an outlet and a funnel, a mixture of 5.2 g. of cuprous bromide and 20 ml. of 48 per cent hydrobromic acid was heated to boiling. The diazonium solution was slowly run into the flask through the funnel. Steam distillation followed. The 15 g. (0.048 mole) of crude product obtained was dissolved in 100 ml. of ether and washed with 5 ml. portions of 60 per cent sulfuric acid, water, 5 per cent sodium hydroxide and finally water. The ether solution was dried over magnesium sulfate. The product obtained by evaporation of the ether was twice recrystallized from isopropyl alcohol yielding 7.0 g. (0.022 mole).

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29. K. J. P. Orton and C. Pearson, J. Chem. Soc., 93, 725 (1908).

30. J. L. Hartwell, Organic Syntheses, Coll. Vo. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 185.

Table 2

Boiling Points of Some Chemicals Used

Compound	Observed value	Literature value
Anisole	153.5-154.5°	153.8° (31)
Benzene	79.0-80.0°	80.1° (32)
Bromobenzene		
"student-prep"	155-157°	156.0° (33)
Eastman	154-155°	
m-Bromofluorobenzene	149-150°	150-151° (34)
p-Bromofluorobenzene	152-153°	152-153° (34)
o-Bromofluorobenzene	156-157°	157-158° (34)
m-Bromotoluene	183.0-183.5°	184.0° (35)
o-Bromotoluene	180.5-181.0°	181.0° (36)

31. R. R. Dreisbach, and R. A. Martin, Ind. Eng. Chem., 41, 2875 (1949).

32. A. F. Forziati, A. R. Glasgow, Jr., C. B. Willingham and F. D. Rossini, J. Research Natl. Bur. Standards, 36, 129 (1946).

33. M. A. Zmaczynski, J. chim. phys., 27, 503 (1930).

34. K. Fukui, H. Kitano, T. Osaka, Y. Inamoto and S. Shioji, Nippon Kagaku Zasshi, 79, 1120 (1958); C. A., 54, 5518c (1960).

35. J. M. Stuckey and J. H. Saylor, J. Am. Chem. Soc., 62, 2922 (1940).

36. W. H. Perkin, J. Chem. Soc., 69, 1025 (1896).

Table 3

Boiling Points of Some Chemicals Used

Compound	Observed value	Literature value
Chlorobenzene	131-132°	131.7° (33)
Ethylbenzene	134-135°	136.2° (37)
Fluorobenzene	84-85°	84.8° (38)
Isoöctane	98-99°	99.2° (32)
Toluene	110-111°	110.6° (32)
m-Xylene	136-137°	139.1° (32)
p-Xylene	136-137°	138.3° (32)
o-Xylene	143-144°	144.0° (32)

37. L. C. Gibbons, J. F. Thompson, T. W. Reynolds, J. I. Wright, H. H. Chanan, J. M. Lamberti, H. F. Hipsher and J. V. Karabinos, J. Am. Chem. Soc., 68, 1130 (1946).

38. E. M. Moore and M. E. Hobbs, ibid., 71, 411 (1949).

Table 4

Melting Points of Some Chemicals Used

Compound	Observed value	Literature value
p-Bromotoluene	27.5-28.0°	26.7° (39)
p-Dibromobenzene	87.0-88.0°	87.3° (40)
p-Dichlorobenzene	53.0-54.0°	53.1° (31)
Diphenyl ether	27.0-28.0°	26.9° (31)
1,2,4-Tribromobenzene	42.5-43.0°	44.0° (28)
1,2,3-Tribromobenzene	86.0-88.0°	87.4° (41)

39. H. van der Laan, Rec. trav. chim., 26, 17 (1907).

40. A. N. Campbell and L. A. Prodan, J. Am. Chem. Soc., 70, 553 (1948).

41. E. Repossi, Z. Kryst. Min., 46, 402 (1908-9).

Instrumentation

Gas-Liquid Chromatography Instruments.--Two Perkin-Elmer Vapor Fractometers Model 154-D, were used. One instrument was a standard unit and was used with all runs involving packed columns. The other was equipped with a Perkin-Elmer hydrogen flame ionization detector (accessory kit 154-0410) and was used only for work with the Golay columns. Helium was used as the carrier gas with the packed columns and nitrogen was used with the Golay columns. The recommended operating procedures were used with both instruments.

Gas-Liquid Chromatography Columns.--All columns used were standard Perkin-Elmer commercial products. All the packed columns with the exception of the preparative column were made of 1/4 inch stainless steel tubing two meters in length. The preparative column was constructed of one inch aluminum tubing. Each capillary column was a Perkin-Elmer Golay column 300 feet in length with an inside diameter of 0.010 inch. The columns are described in Table 5. The word "packed" will be omitted in referring to packed columns in any following descriptions.

Distillation Columns.--Four distillation columns were used. Column No. 1 was an Ace Glass Incorporated commercial product. The body of the column, packed with glass helices, was vacuum-jacketed and approximately two feet in length with an inside diameter of about two cm. Column No. 2 was a 17 by 1.5 cm. Vigreux. Column No. 3 was a 53 by 2 cm. Vigreux. The body of column No. 4, containing tantalum Heli-grid packing, was vacuum-jacketed and 12 inches in length.

Infrared Measurements.--All of the infrared measurements were made using a Perkin-Elmer Recording Spectrophotometer, Model 21. All quantitative

Table 5

Description of Gas-Liquid Chromatography Columns

Column	Liquid Phase	P. E. Parts No.
C	Dimethylsiloxane polymer	154-0013 Cx
K	Polyethylene glycol	154-0013 Kx
O	Silicone grease	154-0013 Ox
P	Succinate polyester of diethylene glycol	154-0013 Px
R	Polypropylene glycol	154-0013 Rx
Q	Apiezon "L" grease	154-0013 Qx
U	"Squalane"	154-0013 Ux
Preparative O	Silicone grease	154-0106
Golay R	Polypropylene glycol	154-0456
Golay Q	Apiezon "L" grease	154-0581

analyses were made in isoöctane at a constant wave length and with the slit width set manually to the value obtained at that wave length with an automatic slit control setting 987. Sodium chloride 0.0185 cm. cells were used. Pure isoöctane was used in the reference beam in all runs unless it is stated otherwise.

Constant Temperature Baths.--A Sargent constant-temperature water bath was used for temperatures of 25.0° and 35.0°. Any variation in the temperature of the bath was not noticeable on a thermometer graduated in tenths of a degree. The temperature of 35.0° was adjusted to 35.0° ± 0.2° using a -10° to 100° thermometer with 0.5° divisions and certified by the National Bureau of Standards. An oil bath was used for temperature 53.5 ± 0.50°. Refluxing water was used for 99.5°.

Melting Point and Boiling Point Determinations.--Melting points were determined in capillary tubes in a circulating oil bath. Boiling points were taken as the distillation temperature of the fraction collected. All boiling and melting points reported herein are uncorrected.

Quantitative Gas-Liquid Chromatography.

Two methods were used for the quantitative calculation (42) of the mole per cent composition of the samples. In cases where standard samples were not available it was necessary to use the method of internal normalization.[4] In this method the area under each peak is assumed

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[4]The normalized value for A_i (A_i^n) is calculated using the formula $A_i^n = 100(A_i/\Sigma A_i)$; therefore $\Sigma A_i^n = 100$.

42. A. I. M. Keulemans, Gas Chromatography, 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1959, p. 35.

to be proportional to mole fraction of the component represented. Therefore, dividing each area by the total area gives the mole fraction of each component. The area was measured as the product of the peak height times the width of the peak at half height.

In nearly all runs the equilibrium samples represented a small concentration range and peak height versus concentration relationships were used when standard samples were available. This method was chosen over the recommended (42) use of peak area versus concentration relationships because the peak obtained for benzene was usually very narrow and there was considerable error involved in measuring its width. Standard samples were prepared having concentrations of the various components approximately equal to those in the equilibrium samples. The standards were run on the chromatograph along with the samples from the equilibrium reactions. Peak heights were measured from the base line to the peak maximum. The peak height versus concentration relationships could be expressed in the form of a graph. However, since the concentration ranges used generally were small, mole per cent/cm. factors were usually calculated directly from the data. An average factor for each component was calculated using the peak heights obtained for the standard samples. The peak height for each component in a sample to be analyzed was multiplied by the appropriate factor. This multiplication yielded mole per cent composition values. When a mole per cent value was obtained for each of the desired components the sum would be expected to be 100. However, due to the fact that the samples from the reaction mixture usually contained small amounts of high boiling compounds and due to small

variations in the size of the sample introduced into the chromatograph, the total was seldom exactly 100. Therefore the values were normalized. Normalization does not, of course, change any of the relative values such as disproportionation constants or meta/para ratios but it does add to the convenience of handling the data.

In most determinations several of the prepared standard samples were not used for calibration purposes but were used as control samples to test the dependability of the analysis.

Treatment of the Data

The mole per cent concentrations obtained were used in certain calculations. Disproportionation constants for the reaction

$$C_6H_5X + C_6H_5Y \rightleftharpoons C_6H_6 + C_6H_4XY$$

were calculated using the formula[5]

$$K_d = [C_6H_6][XC_6H_4Y]/[C_6H_5Y][C_6H_5X]$$

Disproportionation and Isomerization Reactions

Disproportionation of Bromobenzene (9) and Isomerization of p-Dibromobenzene.--A number of experiments on the disproportionation of bromobenzene were carried out. The general technique involved adding the desired quantities of benzene, bromobenzene or dibromobenzene to a flask

[5]Although disproportionation usually refers only to the case in which X and Y are the same, the ratio shown will be referred to as a disproportionation constant.

under nitrogen. Aluminum bromide was then added by holding an ampoule above the flask by the "handling tip" with pliers. The tip was crushed and the ampoule fell into the flask. Vigrous shaking of the flask completed breaking the ampoule and effected solution of the aluminum bromide in about fifteen minutes.

Each solution containing benzene became pale yellow when the aluminum bromide dissolved.[6] All solutions turned to an opaque reddish-brown in several hours but apparently remained homogeneous. Unless otherwise stated each solution went through a period of green color.

Two types of containers were used for placing the reaction mixtures in a constant temperature bath. A long-neck flask fitted with a ground-glass stopper was used in each case unless it is stated that sealed glass tubes were used.

Sampling involved the withdrawal of about three ml. from a container under a stream of nitrogen. This three ml. was run into a centrifuge tube containing about three ml. of 5 per cent hydrochloric acid and some crushed ice. After shaking the tube to destroy the aluminum bromide in the organic phase, the phases were separated using a centrifuge. The organic layer was withdrawn and dried over about 0.1 g. of magnesium sulfate.

Samples for analysis were taken from the experiments listed in Table 6. Experiments Nos. 1-9 were carried out in an exploratory

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[6]Brown and Wallace (10), who made a careful study of the properties of solutions of aluminum bromide in aromatic hydrocarbons, reported the benzene solution to be yellow.

Table 6

Quantities of Materials Used

in Experiments on the Disproportionation of Bromobenzene

Experiment	Al_2Br_6 g.	Al_2Br_6 mmole	Benzene ml.	Benzene mmole	Bromobenzene ml.	Bromobenzene mmole	Dibromobenzene g.	Dibromobenzene mmole
No. 1	2.6	5			50	480		
2	2.9	5	5	56	100	960		
3	2.9	5	10	112	50	480		
4	2.9	5	75	840			32.7[a]	140
5	11.0	23	10	112	50	480		
6	4.9	9	20	225	100	960		
7	3.9	8	5	56	100	960		
8	3.0	6	25	282			50[b]	210
9	3.8	7					50[a]	210
10	5.0	9			50	480		

[a] *Para* isomer.

[b] *Meta* isomer, 25 ml.

manner and were not designed to yield highly accurate results. Experiment No. 10 was designed to give more accurate results for the disportionation constants of bromobenzene.

Experiments Nos. 1-8 in which the "student-prep" bromobenzene and undistilled m-dibromobenzene were used, were carried out at 25.0° with the exception of No. 7. The solution prepared in experiment No. 7 was divided into eight glass tubes. Four of these were run at 53.5° and four at 99.5° The analyses of experiments Nos. 1-7 were carried out using two g.l.c. columns. Preliminary analysis for high boiling components was done using column O at 184° and 15 p.s.i. Retention times as measured to the peak maxima were 22 minutes for 1,2,4,5,-tetrabromobenzene, 8 min. for 1,2,4- and 7 min. for 1,2,3-tribromobenzene. Several standard samples were run for comparison with the samples to be analyzed. No tetrabromobenzenes were detected and the only tribromobenzene found was the 1,2,4 isomer, which was present in low concentrations as shown in Table 7.

Table 7

Concentrations of 1,2,4-Tribromobenzene in Several Experiments

Sample	Temp.	Time	Mole %
Exp. No. 1	25.0°	22 days	0.08
2	25.0°	22 days	0.02
5	25.0°	20 days	>0.01
7	99.5°	3 hrs.	0.17
7	53.5°	3 days	0.09
Control Sample 12-30			
Found			0.47
Prepd.			0.42

The main analysis was carried out using packed column K at 174° and 20 p.s.i. The retention times were 52 sec. for benzene, 2 min. for bromobenzene, 10.25 min. for m-, 11 min. for p- and 13.5 min. for o-dibromobenzene. There was good separation of the ortho and para peaks, but the meta and para peaks overlapped considerably. A number of standard samples were prepared and run on the chromatograph along with the unknown samples. Mole per cent versus peak height graphs were used to determine the compositions of the unknown samples using the observed peak heights.

The analysis of the samples from experiment No. 8 was carried out using g.l.c. column R at 175° and 25 p.s.i. The retention times were 1 min. for benzene, 4 min. for bromobenzene, 14 min. for m-, 14.5 min. for p- and 17 min. for o-dibromobenzene. The separations were essentially the same as those obtained on column K. Several standard samples were prepared to be of approximately the same concentration as the equilibrium samples. Mole per cent per cm. factors were used.

Samples were taken in experiment No. 6 to follow the course of the disproportionation reaction. The results, shown in Table 8, Table 9 and Fig. 1, show that p-dibromobenzene is formed more rapidly than the meta isomer but undergoes a slow isomerization to give the equilibrium meta/para ratio of about 1.9.

The average values of some constants found in the experiments carried out at 25.0° are given in Table 10. The values were obtained by averaging the results of two of more consecutive samples. The assumption that the reactions had reached equilibrium was based on the constancy of

Table 8

Disproportionation of Bromobenzene at 25.0°, Experiment No. 6

Time	Benzene	Bromo-benzene	Dibromobenzene		
			m	p	o-
0	17.8	82.2			
1/2 hr.	17.2	82.3		0.3	0.09
2 hrs.	18.0	79.9	>0.1	1.7	0.4
6 hrs.	20.9	74.6	0.3	3.8	0.6
12 hrs.	22.5	71.2	1.7	4.2	0.5
2 days	24.5	68.1	3.2	3.7	0.5
14 days	27.2	63.4	5.7	3.0	0.4
20 days	29.3	62.3	5.4	2.7	0.3

Table 9

Disproportionation of Bromobenzene at 25.0°, Experiment No. 6

Time	K_d(meta)	K_d(para)	Meta/para	Ortho/para	Per cent reaction[a]
0					
1/2 hr.		0.0007		0.33	2
2 hrs.		0.0048		0.23	9
6 hrs.	0.0011	0.0141	0.08	0.15	27
12 hrs.	0.0076	0.0185	0.40	0.12	41
2 days	0.0167	0.0197	0.85	0.13	61
14 days	0.0387	0.0202	1.92	0.14	96
20 days	0.0408	0.0207	1.97	0.12	100

[a] Per cent reaction $= \frac{K_d}{K_{d(equil.)}} \cdot (100)$ where $K_d = \frac{[C_6H_6][o,m- \text{ \& } p\text{-}C_6H_4Br_2]}{[C_6H_5Br]^2}$

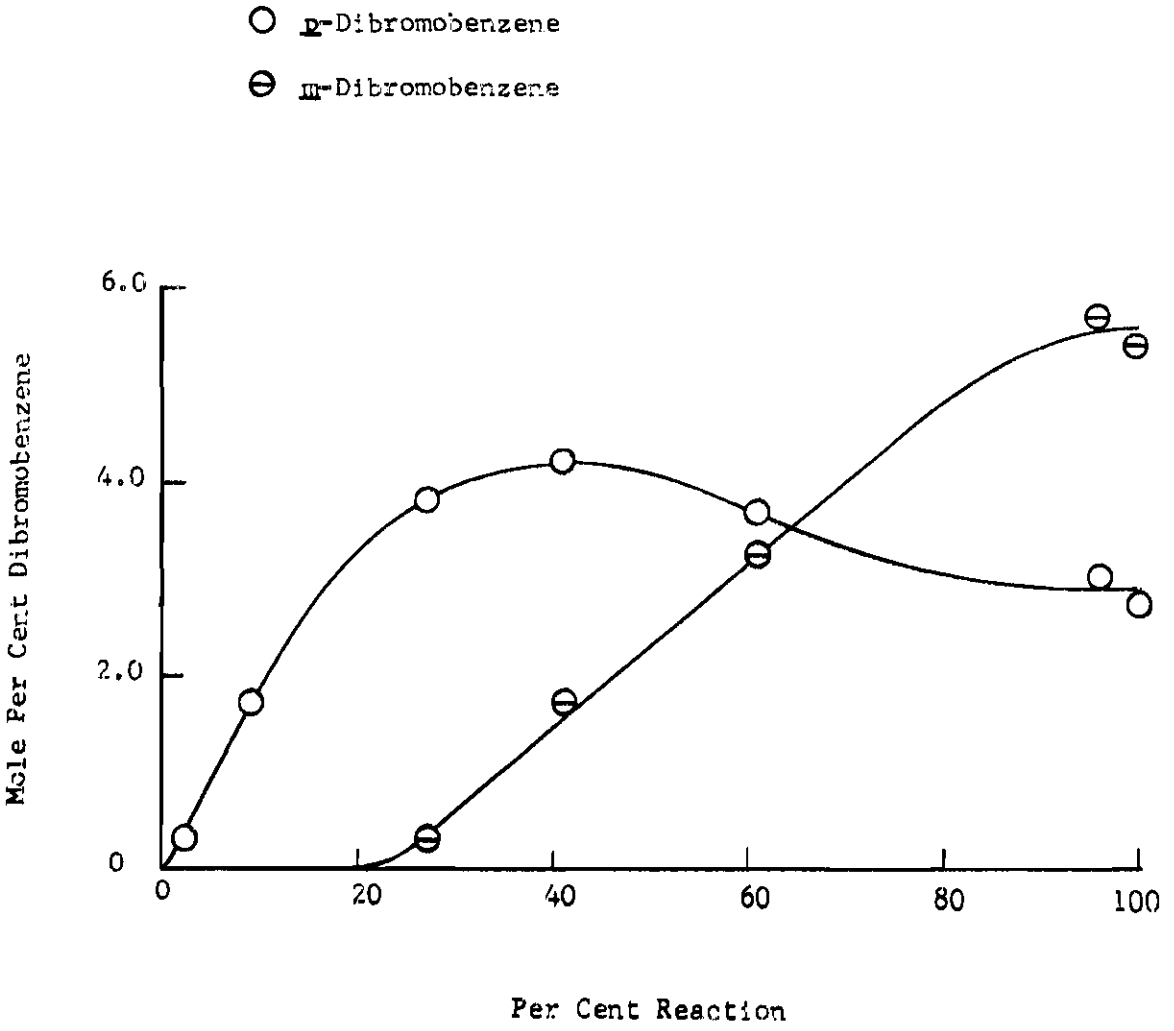

Fig. 1. Mole Per Cent m- or p-Dibromobenzene vs. Per Cent Reaction in the Disproportionation of Bromobenzene, Experiment No. 6.

Table 10

Disproportionation of Bromobenzene[a] at 25.0°, 53.5° and 99.5°

Experiment	Temp.	K_d(meta)	K_d(para)	Meta/para
No. 1[b]	25.0°	0.0404	0.0213	1.90
No. 2[c]	"	0.0426	0.0225	1.90
No. 3[c]	"	0.0382	0.0210	1.81
No. 5[c]	"	0.0383	0.0200	1.92
No. 6[c]	"	0.0398	0.0205	1.95
No. 4[d]	"	0.0450	0.0240	1.87
No. 8[e]	"	0.0356	0.0181	1.97
Av.	"	0.0400 ± 0.0023	0.0211 ± 0.0013	1.90 ± 0.04
No. 7[c]	53.5°	0.0471 ± 0.0034	0.0249 ± 0.0020	1.90 ± 0.02
No. 7[c]	99.5°	0.0556 ± 0.0021	0.0286 ± 0.0021	1.93 ± 0.03

[a]The values shown here are averages of two or more consecutive samples showing a nearly constant composition. See Tables 37 and 38 for more detailed data.

[b]Starting with bromobenzene.

[c]Starting with bromobenzene and benzene.

[d]Starting with p-dibromobenzene and benzene.

[e]Starting with m-dibromobenzene and benzene.

results on consecutive runs and a prior estimate of the equilibrium values from preliminary runs. Furthermore, to prove that equilibrium had been reached, the equilibrium was approached from both sides. In experiments Nos. 1, 2, 3, 5, and 6 bromobenzene was used as a reactant, in experiment No. 8 m-dibromobenzene and benzene were used and in experiment No. 4 p-dibromobenzene and benzene were used as starting materials. Essentially the same equilibrium constants were reached from either direction showing that the reactions had indeed reached equilibrium.

These results also show that the equilibrium constants are not greatly affected by the aluminum bromide concentration; in experiment No. 2 the concentration of aluminum bromide per mole of bromobenzene was 0.0055 and in experiment No. 5 it was 0.047. Also, the benzene concentration did not affect the results. In the equilibrium solutions the benzene concentrations varied from around 17 per cent in experiment No. 1 to as high as 72 per cent in experiment No. 4 and no trend in the equilibrium constants was found.

The results obtained in experiment No. 7, given in Table 10, show that the disproportionation constants are increased by an increase in temperature. The meta/para ratio is also increased slightly, approaching a more random distribution. The heat of reaction and the entropy change for the reaction were calculated (see Appendix) from these data. Also, it was shown that the difference between ΔS° for the disproportionation to m- and p-dibromobenzene is due to the contribution of statistical factors.

In order to obtain more accurate data on the disproportionation constants of bromobenzene experiment No. 10 was carried out. Eastman

white label bromobenzene and distilled m-dibromobenzene were used. The reaction mixture consisted of 50 ml. (0.48 mole) of bromobenzene and 5 g. (0.009 mole) of aluminum bromide. The reaction temperature was 35.0°. The analysis was carried out using a Golay column Q at 175° and 30 p.s.i. The retention times were 12.5 min. for benzene, 14.6 min. for bromobenzene, 23 min. for m-, 23.6 min. for p- and 25.4 min. for o-dibromobenzene. The Golay column gives much sharper peaks than the packed columns and even though the difference in retention times for m- and p-dibromobenzene was less with the Golay column the separation was much better. There was, however, still some overlap of their peaks.

Standard samples were prepared containing benzene, bromobenzene, m-, p- and (in some cases) o-dibromobenzene in approximately the same concentrations as the equilibrium mixture. Several of these standards were used to calculate mole per cent per cm. factors and two others were used as control samples to check the accuracy of the method. Instead of averaging the factors for the entire run, as was done in the two previous analyses, the factors were averaged over a shorter period of continuous operation. A typical period, one morning, included two standards and five samples. The samples run in a given period were calculated using only the factors obtained from the standards run in that period. This method was adopted because of the observed unavoidable fluctuations in temperature, flow rate and other operating parameters.

The results of experiment No. 10 are given in Table 11. The results on the control samples 4-11-2 and 4-11-4, which were not included in the calibration, gave an idea of the ability of the method to analyze unknown samples. For control sample 4-11-2, which shows the larger

Table 11

Disproportionation of Bromobenzene at 35.0°[a]

Sample	K_d(meta) 10^2	K_d(para) 10^2	Meta/para	Ortho/para
1 day[b]	3.714	1.909	1.948	0.1540
2 days[b]	3.671	1.874	1.959	0.1488
3 days	3.705	1.871	1.980	0.1476
4 days	3.750	1.904	1.970	0.1532
Av.[c]	3.699 ± 0.053	1.886 ± 0.029	1.962 ± 0.021	0.1505
Control Sample (4-11-4)				
Found[a]	4.376 ± 0.032	2.146 ± 0.021	2.022 ± 0.004	0.1479
Prepd.	4.403	2.173	2.026	0.1488
Control Sample (4-11-2)				
Found[a]	4.061 ± 0.128	2.060 ± 0.069	1.972 ± 0.009	---
Prepd.	4.161	2.116	1.967	---

[a]Data from Experiment No. 10.

[b]Average of several determinations.

[c]Average of 18 determinations.

differences in the experimental and prepared values, the experimental values for K_d(meta) and K_d(para) were 2.5 and 2.6 per cent higher, respectively, than the prepared values. The observed meta/para ratios are within less than one per cent of the prepared values. The average deviation of the experimental mole per cent and disproportionation constants are on the order of 1 per cent. The average values found, K_d(meta) 0.0370, K_d(para) 0.0189 and meta/para 1.962 are in general agreement with the less accurate results listed in Table 10. These results also are in general agreement with the approximate disproportionation constant, 0.04, given by Fairbrother and Scott (9). However, these workers reported that the dibromide appeared to consist chiefly of the para isomer, indicating that their reactions had not reached isomerization equilibrium.

Experiment No. 9 was carried out to study the mechanism of the isomerization of the dibromobenzenes. The method was similar to that used by McCaulay and Lien (25) in studying the isomerization of the xylenes. Aluminum bromide (0.007 mole) was added to melted p-dibromobenzene (0.21 mole) maintained at a temperature of about 100°. Samples, withdrawn using a pipette wrapped in heating tape, were shaken with ice water and dissolved in chloroform. The analysis was carried out using a g.l.c. column R at 175° and 25 p.s.i. The results, given in Table 12, show the ortho/para ratio had almost reached its equilibrium value before a detectable amount of the meta isomer was formed. Considerable disproportionation of the p-dibromobenzene into benzene, bromobenzene and tribromobenzenes occurred but their concentrations were not determined.

Table 12

Isomerization of p-Dibromobenzene[a]

Time, min.	Dibromobenzene, % o-	m-	p-	Ortho/para	Meta/para
0			100		
1	6	>5	94	0.06	0.05
10	16	>5	84	0.16	0.05
20	8	53	39	0.21	1.37
30	7	61	32	0.21	1.90

[a]Data from experiment No. 9.

The Attempted Disproportionation of Chlorobenzene and the Isomerization of p-Dichlorobenzenes.--The disproportionation of chlorobenzene was attempted in experiment No. 11, in which 50 ml. (0.49 mole) of chlorobenzene and 3 g. (0.012 mole) of aluminum bromide were mixed. The solution was heated overnight at 100° in a sealed tube. The analysis was carried out using a g.l.c. column R at 150° and 30 p.s.i. Benzene and dichlorobenzenes were detected in concentrations of about 1 per cent each. Chlorobenzene is therefore rather inert to reaction conditions that caused bromobenzene to undergo disproportionation very rapidly. This result is in agreement with the report (20) that very little disproportionation accompanies the isomerization of the dichlorobenzenes using aluminum chloride at 160° for 50 hours.

Experiment No. 12 was designed to study the isomerization of the dichlorobenzenes. To 60 g. (0.41 mole) of p-dichlorobenzenes and 40 ml.

(0.39 mole) of chlorobenzene heated to 100° under nitrogen was added 8.0 g. (0.030 mole) of aluminum chloride. In about 10 minutes the aluminum chloride had dissolved.[7] The hot solution was divided, using a pipette wrapped in heating tape, into glass tubes which were then sealed and heated for various lengths of time at 170-190°. A tube to be sampled was cooled and the contents shaken with 5 per cent hydrochloric acid and ice, separated from the aqueous layer, and dried over magnesium sulfate. The analysis was carried out using packed column R at 102° and 30. p.s.i. The retention times were 2 min. for benzene, 7.8 min. for chlorobenzene, 22.7 min for *m*-, 24.8 min. for *p*- and 29 min. for

Table 13

Isomer Distribution in the Isomerization of *p*-Dichlorobenzene[a]

Time hrs.	Temp.	Dichlorobenzene, % *o*-	*m*	*p*-	Ortho/meta	Per cent reaction[b]
0				100		
0.5	170°	)0.2	1.0	99.0	)0.02	1.4
3	170°	0.6	12.5	87.5	0.05	18
3	190°	1.8	38.2	60.0	0.05	58
8	190	2.3	48.5	49.2	0.05	74
Equil.[c] Value	180°	13	56	31	0.23	100

[a]Benzene, chlorobenzene and dichlorobenzene distribution given in Table 40.

[b]Per cent reaction = $\frac{100 - [\%\ \text{para}]}{100 - 31}(100)$.

[c]From Spryskov and Erykalov (20).

[7]$AlCl_3$ is not soluble in chlorobenzene at room temperature.

o-dichlorobenzene. The meta and para peaks overlapped to a small extent. No standard samples were prepared, so the method of internal normalization was used to calculate the compositions of the samples. The results, listed in Table 13 show that the ortho/meta ratio is approached from the low side and never exceeded its equilibrium value (21) of 0.23.

Disproportionation of Toluene.--A number of attempts to obtain a satisfactory disproportionation equilibrium for toluene were carrried out. The following is a typical experiment.

In experiment No. 13, 40 ml. (0.037 mole) of toluene, 20 ml. (0.226 mole) of benzene and 7.64 g. (0.15 mole) of aluminum bromide were mixed and put into glass tubes. Hydrogen bromide was bubbled in and a dark red oil (10) separated. Hydrogen bromide addition was continued until no further formation of the heavy oil was observed. The tubes were sealed and placed in a flask of refluxing water. Agitation of the tube was accomplished in the following manner. One end of the tube was kept at water level by means of a cork. The sealed end was raised and lowered by means of a wire attached through a condenser to an off-center pivot on a 35 r.p.m. motor. The mixing of the two phases was fair.

After cooling and opening a sealed tube, it was centrifuged to separate the oil layer, which contains the complexed hydrocarbons. The top hydrocarbon layer was withdrawn, shaken with 5 per cent hydrochloric acid and some ice and dried over magnesium sulfate.

The analysis was carried out using a g.l.c. column R at 110° and 20 p.s.i. The retention times were 3 min. for benzene, 6 min. for toluene, 10.5 min. for m- and p-xylene and 12.5 min. for o-xylene. The m- and p-xylene isomers were not separated. No standard samples were

prepared. Concentrations were calculated using the method of internal normalization. Since isomerization among the xylenes is known (17) to be much faster than the disproportionation it was assumed that the xylenes formed were of equilibrium composition and thus the xylene fraction represented by the meta-para peak had a meta/para ratio of 2.9 (15).

Toluene was found to undergo disproportionation at a relatively slow rate. Preliminary experiments showed that essentially no reaction occurred in mixtures of toluene, aluminum bromide and hydrogen bromide stirred for a week at room temperature. Thus higher temperatures were used as in experiment No. 13. However, the reaction was still extremely slow for after 13 days in refluxing water a K_d(meta) value of only 0.05 was found.[8] Furthermore, ethylbenzene was found to be formed along with the xylenes,[9] appearing as a shoulder on the meta-para peak. Therefore, due to these complications no equilibrium values for the disproportionation of toluene were obtained.

Disproportionation of Ethylbenzene.--Samples were taken in the following experiments. In experiment No. 14, 7.2 ml. (0.08 mole) of benzene, 40 ml. (0.33 mole) of ethylbenzene and 0.75 g. (0.003 mole) of alumnium chloride were mixed under nitrogen. In experiment No. 15, 20 ml. (0.13 mole) of diethylbenzene, consisting of the meta and para isomers with a meta/para

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[8] The data of Pitzer and Scott (11) gives a value of about 0.14 and that of Taylor, et al, (13) gives 0.20.

[9] The interconversion of the xylenes and ethylbenzene is accomplished in industrial processes, for example, over platinum on deactivated silica-alumina at temperatures around 450° (43).

46. P. M. Pitts, Jr., J. E. Connor and L. N. Leum, Ind. Eng. Chem., 47, 770 (1955).

ratio of about 1.18, 16 ml. (0.18 mole) of benzene and 0.50 g. (0.0019 mole) of aluminum chloride were used. Hydrogen bromide was bubbled into each mixture. The aluminum chloride dissolved giving a small amount of a heavy dark-yellow oil. Each reaction was carried out 35.0° in a stoppered flask. In experiment No. 16, 5.36 g. (0.05 mole) of m-diethylbenzene and 4.7 g. (0.06 mole) of benzene containing 0.001 mole of aluminum bromide were mixed and put into glass tubes. After bubbling hydrogen bromide into the tubes, they were sealed and put into the 35.0° bath.

Agitation of the tubes was accomplised by attaching them to a glass rod which was turned by an 18 r.p.m. motor. The contents of one of the flasks were mixed by periodical manual shaking while in experiment No. 15 stirring was done with a magnetic bar. This was accomplished by placing the flask in a 1-liter beaker containing water thermostated at 35.0° by pumping water from the bath through a copper coil in the beaker. To take a sample, agitation was stopped and when the heavy oil layer separated about three ml. of the hydrocarbon layer was withdrawn. The sample was treated with 5 per cent hydrochloric acid and ice, separated from the aqueous phase and dried over magnesium sulfate. It was observed that the reaction had proceeded very little in two days without stirring but reached equilibrium in about one day with stirring.

When the Golay column O was new it appeared that all the components in the equilibrium mixture could be determined in one run at 125° and 30 p.s.i. The retention times were 8.5 min. for benzene, 10.8 min. for ethylbenzene, 17.5 min. for m-, 18.5 min. for p- and about 18.6 min. for o-diethylbenzene. The meta and para isomers were separated and the

ortho appeared as a shoulder on the para peak. However, after using the column for several days the o-diethylbenzene peak was no longer distinquishable due to a slight broadening of the para peak. By the use of standard samples it was shown, however, that the ortho did not interfere with the para peak height. Thus all components except the o-diethylbenzenes were determined using Golay column Q at 125° and 30 p.s.i. Eight standard samples were prepared to be of approximately the same concentrations as the equilibrium samples. Three were used as control samples and five were used to calculate mole per cent per cm. factors. The o-diethylbenzene concentration was estimated using column P at 103° and 20 p.s.i. The retention times were 1.5 min. for benzene, 3 min. for ethylbenzene, 6.5 min. for m- and p-diethylbenzene and 7.5 min. for o-diethylbenzene. The ortho peak was not completely separated from the meta-para peak. Several standards were run along with the samples and mole per cent per cm. factors were determined for ethylbenzene and o-diethylbenzene. An o-diethylbenzene-ethylbenzene ratio was determined for a given sample and multiplied by the ethylbenzene concentration found for that sample by analysis on the Golay column. This gave concentration values for all the desired components so the values were normalized.

Ethylbenzene was found to undergo disproportionation readily. The equilibrium data are given in Table 14. About 1 per cent of a high boiling compound, probably a triethylbenzene, was also present but was not included in the analysis. The use of the different reactants in the three experiments was designed to approach the equilibrium values from both high and low sides. Essentially the same values were obtained in all three experiments and thus the reactions had reached equilibrium.

Table 14

Disproportionation of Ethylbenzene at 35.0°

Sample	K_d(meta)	K_d(para)	Meta/para	Ortho/para
Exp. No. 14				
8 days[a]	0.160 ± 0.001	0.0693 ± 0.0006	2.31 ± 0.01	0.10
Exp. No. 15				
3 days[a]	0.159 ± 0.002	0.0698 ± 0.0004	2.28 ± 0.01	0.12
Exp. No. 16				
6 days[a]	0.161 ± 0.001	0.0697 ± 0.0001	2.31 ± 0.01	0.11
Av.[b]	0.160 ± 0.001	0.0693 ± 0.0003	2.31 ± 0.01	0.11
Control Sample (1-24-8)				
Found[a]	0.209 ± 0.003	0.0933 ± 0.0013	2.24 ± 0.03	--
Prepd.	0.2071	0.0929	2.23	--
Control Sample (1-24-1)				
Found[a]	0.211 ± 0.002	0.0938 ± 0.0008	2.25 ± 0.01	0.164
Prepd.	0.2126	0.0944	2.25	0.158
Control Sample (1-24-2)				
Found[a]	0.210 ± 0.001	0.0917 ± 0.0012	2.30 ± 0.03	0.103
Prepd.	0.2132	0.0933	2.28	0.102

[a]Average of several determinations.

[b]Average of 15 determinations.

The data on the control samples are also listed. The average deviations of the disproportionation constants and the meta/para ratios are on the order of 1 per cent. For control sample 1-24-2, which shows the largest differences between observed and prepared values, K_d(meta) observed is 1.3 per cent lower than the prepared value and the observed meta/para ratio is less than 1 per cent higher than the prepared value.

In order to determine the relative rates of the disproportionation of ethylbenzene and the isomerization of the diethylbenzenes the following two experiments were run. In experiment No. 17, 10 ml. (0.11 mole) of benzene, 30 ml. (0.25 mole) of ethylbenzene and 0.44 g. (0.0015 mole) of aluminum chloride were mixed. In experiment No. 18, 20 ml. (0.13 mole) of diethylbenzene (meta/para 1.18), 20 ml. (0.23 mole) of benzene and 0.29 g. (0.001 mole) of aluminum chloride were used. Each solution was stirred at room temperature after the addition of hydrogen bromide. The analysis was carried out using column U at 147° and 25 p.s.i. The retention times were 1 min. for benzene, 3.8 min. for ethylbenzene, 11 min. for m-diethylbenzene and 11.8 min. for p-diethylbenzene. The concentrations were estimated by the internal normalization method.

The data listed in Table 15 show that the meta/para ratio approaches equilibrium faster than the disproportionation constant does. In experiment No. 18, in which diethylbenzene and benzene were used, the equilibrium meta/para ratio is reached while the disproportionation constants are far away from their equilibrium values. In experiment No. 17, in which ethylbenzene and benzene were used, a sample taken at 6.6 per cent reaction had a meta/para ratio 39 per cent of the equilibrium

value and at 47 per cent reaction, 78 per cent.

Table 15

Disproportionation of Ethylbenzene at Room Temperature

Experiment	Time hrs.	K_d(meta)	K_d(para)	Meta/para	Per cent Reaction[a]
No. 17	1[b]	0.008	0.010	0.81	6.6
No. 17	2[c]	0.063	0.035	1.64	47
No. 17	30	0.189	0.091	2.09	100
No. 18	0			1.18	
No. 18	0.08	8.9	6.7	1.35	
No. 18	12	4.9	2.7	1.81	
No. 18	48	4.9	2.7	2.23	

[a]Per cent reaction = $\frac{K_d}{K_d(\text{equil.})}$.

[b]One hour with Al_2Cl_6, before hydrogen bromide added.

[c]One hour after HBr added plus the hour mentioned above.

Reaction of Bromobenzene and Fluorobenzene.--The disproportionation of bromobenzene in the presence of fluorobenzene was found to give o-, m-, and p-bromofluorobenzenes. The dibromobenzenes were also produced, but, as expected, there was no evidence for difluorobenzene formation. Although no difluorobenzene standard was tested, any difluorobenzene present surely would have appeared on some of the many g.l.c. tests that were made. The following solutions were prepared. In experiment No. 19, 15 ml. (0.16 mole) of fluorobenzene, 15 ml. (0.14 mole) of bromobenzene and 6.0 g. (0.113 mole) of aluminum bromide were mixed. In experiment No. 20, 8 ml. (0.090 mole) of benzene, 10 ml. (0.091 mole) of

m-bromofluorobenzene, 0.5 ml. (0.005 mole) of fluorobenzene and 3.5 g. (0.0065 mole) of aluminum bromide was used. This solution took on a deep red color immediately. Experiment No. 21 was identical except that 10 ml. (0.091 mole) of p-bromofluorobenzene were used in place of the meta isomer and the solution was pale yellow. Each solution was put in a long-neck flask fitted with a ground-glass stopper and placed in the 35.0° bath. The sampling procedure was the same as that described for bromobenzene.

No. g.l.c. column was available[10] that would separate all of the components. The concentrations of the dibromobenzenes were not needed and were therefore not determined. The analysis was carried out using two different chromatography runs. The concentrations of m- and p-bromofluorobenzenes and bromobenzene were determined using the Golay column Q at 125° and 30 p.s.i. The retention times were 8.5 min. for benzene and fluorobenzene, 16.4 min. for m-, 16.8 min. for p-, 18.3 min. for o-bromofluorobenzene and 18.5 min. for bromobenzene. Using the packed column P at 90° and 25 p.s.i., benzene, fluorobenzene and o-bromofluorobenzene concentrations were determined. The retention times were 1.3 min. for benzene, 1.6 min. for fluorobenzene, 7.7 min. for m-bromofluorobenzene and 9.5 min. for bromobenzene and p-bromofluorobenzene and 11 min. for o-bromofluorobenzene. The benzene and fluorobenzene peaks were almost completely separated. It was necessary to discontinue runs for about one hour after every three or four samples due to the elution of

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[10] All the columns except Golay column R were available at the time this analysis was made.

the dibromobenzenes.

Eight standards were prepared to be of approximately the same concentrations as the equilibrium samples. Four of these were used to calculate mole per cent per cm. factors and four were used as control samples to check the accuracy. For a given sample, the ratios of m- and p-bromofluorobenzene to bromobenzene were calculated from the runs on the Golay column Q and multiplied by the bromobenzene concentration obtained using the packed column P. The multiplication gave mole per cent concentrations for all the desired components. The concentrations seldom added up to exactly 100 so the values were normalized. The equilibrium values were approached from both sides by using the various components as starting materials in the experiments. Results, given in Table 16, show that the equilibrium values were obtained. The average deviations are on the order of 1 per cent. The largest differences between experimental and prepared values of the control samples were found for sample 3-15-1. The observed K_d(meta) value was 2 per cent lower than the prepared value and the observed K_d(para) value was 2.8 per cent low. The experimental meta/para value was less than 1 per cent high.

Two samples were taken in experiment No. 19 to determine the relative rates of the disproportionation and isomerization reactions. The results, given in Table 17, show that the reaction follows a route similar to that found with bromobenzene itself. Starting with bromobenzene and fluorobenzene an initial build-up of the para and ortho isomers is followed by a slow isomerization to give the equilibrium meta/para ratio of about 2.1.

Table 16

Reaction of Bromobenzene with Fluorobenzene at 35.0°

Sample	K_d(meta)·10^2	K_d(para)·10^2	Meta/para	Ortho/para
Exp. No. 19				
1 wk.[a]	5.945 ± 0.037	2.773 ± 0.017	2.144	0.180
Exp. No. 20				
1 wk.[a]	6.009 ± 0.021	2.849 ± 0.023	2.109	0.186
Exp. No. 21				
1 wk.[a]	5.872 ± 0.013	2.831 ± 0.006	2.075	0.182
Av.[b]	5.953 ± 0.058	2.820 ± 0.030	2.109 ± 0.023	0.183
Control Sample (3-22-5)				
Found[a]	6.371	3.001	2.123	0.232
Prepd.	6.337	3.019	2.099	0.231
Control Sample (3-22-1)				
Found[a]	6.290	2.888	2.178	0.197
Prepd.	6.226	2.864	2.174	0.202
Control Sample (3-15-1)				
Found[a]	4.725	2.381	1.985	0.214
Prepd.	4.823	2.449	1.969	0.222

[a]Average of several determinations.

[b]Average of 19 determinations.

Table 17

Reaction of Bromobenzene with Fluorobenzene at 35.0°[a]

Time, hrs.	K_d(meta)	K_d(para)	Meta/para	Ortho/para	Per cent Reaction[b]
3	0.0023	0.0247	0.09	0.19	34
16	0.0510	0.0283	1.81	0.18	91

[a]Data from experiment No. 19

[b]Per cent reaction = $\frac{K_d}{K_d(\text{equil.})}$.

Reaction of Bromobenzene with Toluene.--The reaction of bromobenzene in the presence of toluene was found to yield bromotoluenes and much smaller concentration of dibromobenzenes. No detectable quantities of xylenes were formed. The following experiments were carried out. In experiment No. 22, 15 ml. (0.169 mole) of benzene, 25 ml. (0.23 mole) of toluene, 15 ml. (0.14 mole) of bromobenzene and 2.5 g. (0.005 mole) of aluminum bromide were mixed. In experiment No. 23, 20 ml. (0.23 mole) of benzene, 5 ml. (0.047 mole) of toulene, 15 ml. (0.12 mole) of m-bromotoluene and 2.5 (0.005 mole) of aluminum bromide were used. The same quantities were used in experiment No. 24 but p-bromotoluene was used instead of the meta isomer. Each solution was put into glass tubes and hydrogen bromide bubbled in until no further formation of a heavy oil layer was observed. The tubes were sealed, placed in a 35.0° bath and wired to a glass rod that was rotated by an 18 r.p.m. motor. Preliminary analysis showed

that the reaction had reached equilibrium in less than four hours. To insure that the temperature of the reaction mixture sampled was as close to 35.0° as possible each opened tube was suspended in the thermostat before withdrawing the top layer. Care was taken not to sample the oil layer. The samples were treated with 5 per cent hydrochloric acid and dried over magnesium sulfate.

No. g.l.c. column available would separate m- and p-bromotoluene. It was necessary to do the analysis in three parts: 1) determination of benzene, toluene, bromobenzene and o-bromotoluene, 2) separation of the bromotoluene fraction and 3) infrared (44) determination of the concentrations of o-, m- and p-bromotoluene. Column P at 102° and 20 p.s.i. was used for the first part of the analysis. The retention times were 1.5 min. for benzene, 2.4 min. for toluene, 9.4 min. for bromobenzene, 13.6 min. for o-bromotoluene and 14.8 min for m- and p-bromotoulene. There was some overlap of the ortho with the meta-para peak. It was observed by superimposing curves of standard samples that the meta-para peak had not started to rise at the position of the ortho peak maximum and therefore would not interfere with this analysis for the ortho isomer. The concentrations of benzene, toluene, bromobenzene and o-bromotoluene were determined using mole per cent per cm. factors, which were obtained using standard samples.

The bromotoluene fraction was separated from the other components using the preparative column O, set for a length of three meters, at 140°

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44. B. R. Cowley, R. O. C. Norman and W. A. Waters, J. Chem. Soc., 1799 (1959).

and 5 p.s.i. The retention times were 2.2 min. for benzene, 3.5 min. for toluene, 6.1 min. for bromobenzene, and 10.2 min. for o-, m- and p-bromotoluene. The bromotoluene fraction gave one symmetrical peak with good separation from bromobenzene. The bromotoluene fraction, collected in a U-tube immersed in dry ice-acetone, was dissolved in isooctane and the concentrations of the isomers were determined by infrared spectroscopy.[11]

For a give sample meta/ortho and para/ortho ratios calculated from the infrared analysis were multiplied by the o-bromotoluene concentration determined using column P. The multiplication gave mole per cent concentrations for all the desired components so the concentration values were normalized.

The results in Table 18 illustrate the reproducibility of the infrared method of determination of the concentrations of the bromotoluene

Table 18

Results of Infrared Analysis
of the Bromotoluene Fraction of Control Sample 8-3-2[a]

	C_m/C_o[b]	C_p/C_o	C_m/C_p
1st. run			
1st. dilution	1.191	0.670	1.779
2nd. dilution	1.195	0.665	1.797
2nd. run	1.198	0.677	1.770
3rd. run	1.202	0.665	1.806

[a] Calculated using 1st-assumption extinction coefficients, details in the Appendix.

[b] C_x = concentration of x-bromotoluene.

[11] Details are given in the Appendix.

isomers. The three runs listed represent the running of three different samples of control sample 8-3-2 through the preparative column O and collection of three different bromotolune fractions.

Average deviations of the constants (shown in Table 19 and 20) found in the experiments are on the order of 1 to 2 per cent. Values determined experimentally for the ratios $[C_6H_6][BrC_6H_4CH_3]/[C_6H_5CH_3][C_6H_5Br]$ for the control samples, Table 21, are 5-10 per cent lower than values calculated from the amounts of materials used to prepare these samples. The meta/para and ortho/para ratios agree with the prepared values within less than 5 per cent.

The equilibrium constants calculated using the assumption that the m- and p-bromotoluene used are not contaminated with each other, Table 19, and the assumption that m-bromotoluene contains 2.1 per cent para isomer and the p-bromotoluene contains 2.3 per cent meta,[12] Table 20, differ by 5 to 10 per cent. Since there is little difference between the results of the two assumptions, the results of the first will be used in further discussions and calculations.

Experiment No. 25, in which 15 ml. (0.17 mole) of benzene, 25 ml. (0.23 mole) of toluene, 15 ml. (0.14 mole) of bromobenzene and 2.0 g. (0.004 mole) of aluminum bromide were used, was carried out to study the course of reaction. After the addition of hydrogen bromide the solution was stirred magnetically in a stoppered flask at room temperature, which was about 28°. To take a sample, the stirrer was stopped and about 3 ml. of the top layer withdrawn and treated in the usual manner.

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[12] The assumptions are discussed in the Appendix.

Table 19

Reaction of Bromobenzene with Toluene at 35.0° [a,b]

Experiment	K_d(meta)	K_d(para)	Meta/para	Ortho/para
No. 22				
1 day	0.5109	0.1845	2.769	2.230
4 days	0.5144	0.1809	2.844	2.295
No. 23				
1 day	0.5167	0.1845	2.801	2.268
4 days	0.5208	0.1931	2.697	2.172
No. 24				
1 day	0.5240	0.1864	2.812	2.303
4 days	0.4974	0.1823	2.728	2.293
Av.	0.5140 ± 0.0066	0.1853 ± 0.0030	2.775 ± 0.044	2.260 ± 0.040

[a]Calculated using the 1st-assumption extinction coefficients for the bromotoluenes, details in the Appendix.

[b]Corresponding concentrations given in Table 43.

Table 20

Reaction of Bromobenzene with Toluene at 35.0° [a, b]

Experiment	K_d(meta)	K_d(para)	Meta/para	Ortho/para
No. 22				
1 day	0.5004	0.1719	2.910	2.394
4 days	0.5036	0.1684	2.993	2.467
No. 23				
1 day	0.5059	0.1717	2.946	2.437
4 days	0.5101	0.1802	2.831	2.328
No. 24				
1 day	0.5129	0.1733	2.959	2.477
4 days	0.4868	0.1696	2.871	2.465
Av.	0.5033 ± 0.0062	0.1725 ± 0.0028	2.919 ± 0.048	2.428 ± 0.045

[a] Calculated using the 2nd-assumption extinction coefficients for the bromotoluenes, details in the Appendix.

[b] Corresponding concentrations given in Table 43.

Table 21

Reaction of Bromobenzene with Toluene at 35.0°

Control Sample	Assumption[a]	K_d(meta)	K_d(para)	Meta/para	Ortho/para
7-26-1					
Found	1st	0.2600	0.1443	1.802	1.022
	2nd	0.2571	0.1389	1.852	1.062
Prepd.	1st	0.2854	0.1461	1.95	1.07
	2nd	0.2826	0.1490	1.90	1.05
8-3-1					
Found	1st	0.3455	0.1630	2.120	1.192
	2nd	0.3413	0.1562	2.184	1.243
Prepd.	1st	0.3843	0.1725	2.23	1.24
	2nd	0.3794	0.1775	2.14	1.21
8-3-2					
Found	1st	0.4025	0.2251	1.788	1.494
	2nd	0.3952	0.2135	1.851	1.576
Prepd.	1st	0.4174	0.2294	1.82	1.56
	2nd	0.4141	0.2327	1.78	1.54

[a]The 1st and 2nd assumptions are discussed in the Appendix.

Table 22

Reaction of Bromobenzene with Toluene at Room Temperature[a]

Time	K_d(meta)	K_d(para)	Meta/para	Ortho/para	Per cent[b] Reaction
5 min.	0.083	0.043	1.9	1.6	17
15 min.	0.144	0.065	2.0	1.8	28
45 min.	0.292	0.146	2.2	1.9	60
4 hrs.	0.541	0.208	2.6	2.1	100

[a]Data were obtained in experiment No. 25.

[b]Per cent reaction = $\frac{K_d}{K_d(\text{equil.})}(100)$:

The results, given in Table 22, show that the isomerization of the bromotoluenes is fast relative to the reaction by which they are formed.

Attempted Reaction of Bromobenzene with Anisole and Diphenyl Ether.--Experiment No. 26 was carried out in the following manner. To a flask containing 10 ml. (0.093 mole) of anisole was added 10 ml. of a freshly prepared solution of 4.80 g. (0.009 mole) of aluminum bromide in 40 ml. (0.38 mole) of bromobenzene. The solution was allowed to react at room temperature. Sampling was done in the manner described for bromobenzene. The analysis was carried out using g.l.c. column C at 125°.and 25 p.s.i. The retention times were 1 min. for benzene, 2.9 min. for anisole, 3.3 min. for phenol, and 3.7 min. for bromobenzene. The peaks were sharp and there was little overlap. The mole per cent results were calculated using the method of internal mormalization.

The bromobenzene-aluminum bromide solution changed from its

characteristic red color to colorless instantly upon addition of the anisole. Fairbrother and Scott (9) reported that a colorless bromobenzene-aluminum bromide solution darkened upon addition of hydrogen bromide. Thus, the loss of the red color was probably due to the destruction of a complex of hydrogen bromide, aluminum bromide and bromobenzene by consumption of hydrogen bromide. No hydrogen bromide was actually added but a small amount was surely produced by hydrolysis of aluminum bromide by moisture present in the system. Furthermore, the results of the analysis, given in Table 23, show that no further reaction to give bromoanisole or dibromobenzene occurred since such formation would have also produced benzene. A separate sample of the original bromobenzene-aluminum bromide solution had reached disproportionation equilibrium, producing about 15 mole per cent benzene, in 24 hrs. These data are explained by a very rapid cleavage of the ether linkage of anisole by aluminum bromide and hydrogen bromide.

Table 23

Attempted Reaction of Bromobenzene with Anisole

Time	Concentration, mole per cent			
	Benzene	Anisole	Bromo-benzene	Phenol
2 hrs.	0.5	49.5	50.0	>0.5
24 hrs.	0.6	48.8	50.6	>0.5

No phenol was detected because only small amounts of hydrogen bromide were involved.

In experiment No. 27 a solution of 10 ml. (0.063 mole) of diphenyl ether and 10 ml. (0.010 mole) of bromobenzene was mixed with 5 ml. of a freshly prepared mixture of 0.90 g. (0.0035 mole) of aluminum chloride and hydrogen bromide in 50 ml. (0.506 mole) of benzene. The latter mixture was prepared by bubbling hydrogen bromide into a stirred mixture until the aluminum chloride dissolved, and the 5 ml. withdrawn while the stirring continued.[13] Samples, withdrawn at time intervals, were washed with water. The analysis was carried out using a packed column Q at 300° and 30 p.s.i. The retention times were 24 sec. for benzene, 42 sec. for phenol, 54 sec. for bromobenzene and 3 min. for diphenyl ether.

A sample take at three minutes showed a peak for benzene, bromobenzene and diphenyl ether. A sample after one hour showed a very much reduced diphenyl ether peak and a new peak, identified as phenol, of about the same size as the bromobenzene peak. The diphenyl ether is therefore cleaved rapidly with aluminum chloride and hydrogen bromide. The fact that no measurable amount of cleavage occurred with anisole but an almost complete cleavage of diphenyl ether occurred is explained by the difference in the amounts of hydrogen bromide present in the reaction solutions. The diphenyl ether reaction was saturated with hydrogen bromide and contained sufficient amounts to cleave most of the ether.

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[13] The oil layer, $(\text{benzene})_x \cdot Al_2X_6 \cdot HBr$ (10), was well dispersed and a representative sample was obtained.

CHAPTER III

DISCUSSION OF RESULTS

Isomerization Studies.--The bromine atom attached to an aromatic ring enters into intermolecular reactions readily as demonstrated by the facile disproportionation of bromobenzene and the fact that considerable disproportionation accompanied the isomerization of p-dibromobenzene. Furthermore, the fact that the formation of the ortho isomer preceded that of the meta isomer in the isomerization of p-dibromobenzene shows that the intermolecular reaction occurs faster than the intramolecular reaction. Therefore, the ortho-meta and para-meta isomerizations probably also proceed by an intermolecular mechanism.

Spryskov and Erykalov (20, 21) suggested that the isomerization of the dichlorobenzenes proceeds by an intermolecular mechanism. Since this would require an electrophilic attack on chlorobenzene, the isomerization of p-dichlorobenzene would proceed with an initial formation of more ortho than meta isomer; an ortho/meta ratio of 11.0 has been reported (26) in the chlorination of chlorobenzene. The equilibrium ortho/meta ratio of 0.23 (21) would be approached from the high side as the kinetically controlled products are isomerized into the thermodynamically more stable products. Increasing the concentration of chlorobenzene in the isomerization solution should increase the possibility that a chlorine atom from p-dichlorobenzene attack chlorobenzene yielding more dichlorobenzene, thus increasing the speed of the intermolecular

isomerization. In experiment No. 12, in which p-dichlorobenzene was isomerized in chlorobenzene, the ortho/meta equilibrium was approached from lower values and never exceeded 0.23. That is, the isomerization of p-dichlorobenzene proceeded with initial formation of the meta isomer.

By the same consideration the isomerization of the o-dichlorobenzene should proceed by initial build-up of the para isomer and the meta/para equilibrium ratio should be approached from the low side. However, the results of Spryskov and Erykalov (20) given in Table 24 show that the meta/para ratio is approached from the high side.

The routes followed by the isomerizations and the fact that the dichlorobenzenes undergo isomerization much more readily than disproportionation cannot be explained by an intermolecular mechanism. These facts are consistent with an intramolecular mechanism for the isomerization.

The results on the bromobenzenes and the chlorobenzenes add support to each other. Bromobenzene was found to undergo disproportionation readily whereas chlorobenzene was relatively unreactive. Considerable disproportionation occurred with the isomerization of p-dibromobenzene but very little accompanied the isomerization of the dichlorobenzenes. These facts alone suggested that the chlorine atom does not enter into intermolecular reactions readily under the conditions used. To support this conclusion the isomerization of p-dibromobenzene was found to proceed with initial formation of the ortho isomer as required for intermolecular mechanism and the isomerization of both p-dichlorobenzene and o-dichlorobenzene proceed with initial formation of the meta isomer as required for the intramolecular mechanism.

Table 24

Isomerization of o-Dichlorobenzene at 160°[a]

Time, hrs.	Dichlorobenzene[b] distribution, % o-	m-	p-	Meta/para	Per cent reaction[c]
0	100				0
5	60.6	29.6	9.8	3.20	47
15	28.0	47.6	24.4	1.95	87
30	20.1	52.3	27.6	1.89	96
50	16.8	54.0	29.2	1.84	100

[a]Data from Spryskov and Erykalov (20).

[b]Less than 1 per cent of chlorobenzene and trichlorobenzenes were present after 50 hrs.

[c]Per cent reaction = $\frac{100 - \%\ [\text{ortho}]}{100 - 16.8}(100)$.

Furthermore, the fact that the xylenes underwent isomerization much faster than disproportionation led to the suggestion (17) that the isomerization proceeded by an intramolecular mechanism. This view has been supported by much experimental work (15, 25, 45, 46).

The shifting of a bromine atom from one ring to another under acidic catalysis, as in a disproportionation reaction or intermolecular isomerization, requires that the bromine atom lose its bonding electrons to the ring which it leaves and gain a new pair from the ring to which it becomes attached. The reaction may be considered to occur by a one-step nucleophilic displacement on the bromine atom involving no charge separation or by a two-step mechanism in which the bromine atom separates from one ring as $Br^{\oplus}$, which then attacks a second ring. The actual mechanism is probably intermediate between these two extremes with the bromine atom acquiring a partial positive charge in the transition state.

This fact explains the difference observed between the bromine and chlorine atoms in disproportionation and isomerization reactions. The bromine atom can better tolerate a positive charge (47), probably by spreading it over a larger volume, and thus enters into intermolecular reactions with greater ease.

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45. H. C. Brown and H. Jungk, J. Am. Chem. Soc., 77, 5579 (1955).

46. H. Steinberg and F. L. J. Sixma, Rec. trav. chim., 81, 185 (1962).

47. R. P. Bell and E. Gelles, J. Chem. Soc., 2734 (1951).

It might be argued that the same factors that increase the intermolecular reactivity would also increase the intramolecular reactivity. In fact, the bromine atom reacts in neighboring-group displacements more readily than the chlorine atom (48). However, the fact that the chlorobenzenes react faster by an intramolecular mechanism than by an intermolecular mechanism but the bromobenzenes react faster by an intermolecular mechanism shows that in going from the chlorine to the bromine atom the rate of the intermolecular reaction is increased more than that of the intramolecular reaction.

In isomerizations of the xylenes in toluene at 50° (15) using 0.25 mole of $Al_2Cl_6 \cdot HCl$ per mole of xylene about forty hours were required to reach equilibrium. Since the bromotoluenes reached isomerization equilibrium in several hours at 35° it is unlikely that a methyl group migration was involved. The fact that the bromotoluenes were isomerized almost as fast as they were formed but the dibromobenzenes and bromofluorobenzenes were isomerized more slowly than they were formed is not proof of an intramolecular shift of the bromine atom in the bromotoluene isomerization. The presence of a methyl group on the ring should not greatly affect the relative rates of the intermolecular and intramolecular migrations of the bromine atom. The faster isomerization of the bromotoluenes may be explained by an intermolecular mechanism. Consider the reactions involved

$$C_6H_5Br + C_6H_5Br \rightleftharpoons C_6H_6 + \underline{o}\text{-}, \underline{m}\text{-} \& \underline{p}\text{-}BrC_6H_4Br \qquad (3\text{-}1)$$

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48. S. Winstein and E. Grunwald, J. Am. Chem. Soc., 70, 828 (1948).

$$\underline{o}\text{- \& } \underline{p}\text{-}BrC_6H_4Br + C_6H_5Br^* \rightleftharpoons C_6H_5Br + \underline{m}\text{-}BrC_6H_4Br^*$$

and

$$C_6H_5Br + C_6H_5CH_3 \rightleftharpoons C_6H_6 + \underline{o}\text{-, } \underline{m}\text{- \& } \underline{p}\text{-}BrC_6H_4CH_3$$

$$\underline{o}\text{- \& } \underline{p}\text{-}BrC_6H_4CH_3 + C_6H_5CH_3^* \rightleftharpoons C_6H_5CH_3 + \underline{m}\text{-}BrC_6H_4CH_3^* \qquad (3\text{-}2)$$

Formation of a disubstituted derivative must proceed via the attack of a proton on bromobenzene. The dibromobenzenes formed are less basic than bromobenzene and are attacked by protons less readily. However, the o- and p-bromotoluenes initially formed in the bromobenzene-toluene reaction are more basic than bromobenzene and are attacked by protons more readily. Once formed, the protonated bromotoluene would most reasonably react with toluene, in a transbromination reaction, to give other bromotoluenes, as in reaction (3-2). Thus, the isomerization equilibrium for the bromotoluenes is established rapidly. The corresponding reaction with protonated dibromobenzene would involve an electrophilic attack on bromobenzene and is therefore not favored. Isomerization of the dibromobenzenes therefore probably proceeds by reversal of the disproportionation reaction (3-1) and reformation of the dibromobenzenes. The arguments used for the dibromobenzenes also apply to the isomerization of the bromofluorobenzenes.

Unseren and Wolf (49) found by carbon-labeling techniques that

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49. E. Unseren and A. P. Wolf, Tetrahedron Letters, No. 19, 691 (1961); J. Org. Chem., 27, 1509 (1962).

when ethylbenzene was treated with aluminum bromide and hydrogen bromide the ethyl group reacted faster by the intermolecular than by the intramolecular mechanism. The ethyl group resembles the bromine atom in this respect. The fact that the isomerization of the diethylbenzenes was fast relative to the reaction by which they were formed could thus be explained in the same terms used to explain the corresponding data on the bromotoluenes if the reactions proceeded by a similar mechanism. However, if the reaction of the diethylbenzenes proceeds by the mechanism given by Streitwieser and co-workers (23, 24), involving the intermediate formation of α-phenethyl cations, the arguments do not apply.

Ortho-Para Ratios.--A summary of some of the constants for the equilibrium reactions is given in Table 25. The small ortho/para ratios for the dibromobenzenes, the bromofluorobenzenes, and the diethylbenzenes are due to a combination of steric interaction and repulsion of like groups. The greater stability of o- over p-bromotoluene, as shown by the ortho/para ratio of 2.26, can be explained by the fact that methyl is inductively electron-donating while the bromine substituent is electron-withdrawing. The inductive effect is a function of distance and therefore more effective for the ortho position. The methyl and bromine substituents therefore stabilize each other most when in an ortho orientation.

Meta-Para Ratios.--The meta/para ratio of 1.96 for the dibromobenzenes shows that the meta and para isomers are of approximately equal stability since a ratio of 2.0 is predicted from purely statistical reasons (two meta positions for one para). The meta/para ratio of 2.11 for the

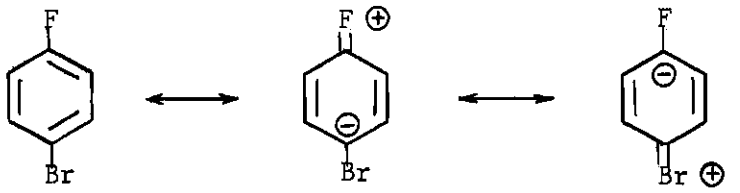
Table 25

Summary of Constants from the Equilibrium Reactions at 35.0°

Reaction	K_d(meta)	K_d(para)	Meta/para	Ortho/para
PhBr-PhBr	0.0370 ± 0.0005	0.0189 ± 0.0003	1.962	0.151
PhBr-PhF	0.0595 ± 0.0004	0.0282 ± 0.0003	2.109	0.183
PhEt-PhEt	0.160 ± 0.001	0.0693 ± 0.0003	2.31	0.108
PhBr-$PhCH_3$	0.5140 ± 0.0066	0.1853 ± 0.0030	2.775	2.260
$PhCH_3$-$PhCH_3$[a]	0.20 ± 0.04	0.076 ± 0.008	2.6	0.9

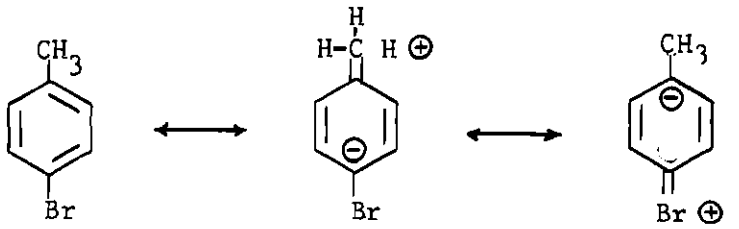
[a]Calculated from the data of Taylor, et al (13).

bromofluorobenzenes shows that the para isomer is slightly destabilized relative to the meta. This result is rather surprising since both resonance structures (II) and (III) should contribute to the stability of the para isomer.



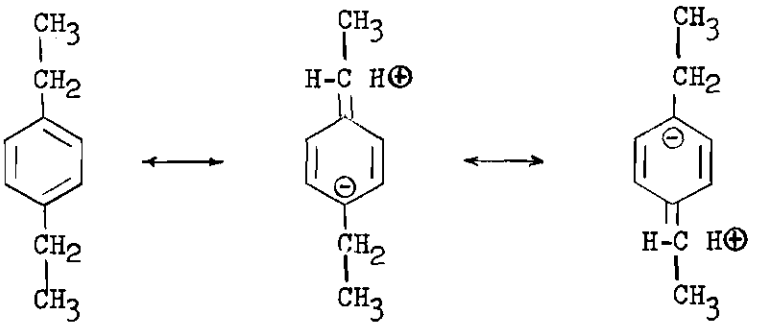
(II) (III)

For the bromotoluenes, structure (IV) should add to the stability of the para isomer but (V) would tend to decrease the stability.



(IV) (V)

The fact that a meta/para ration of 2.775 was found may indicate that structure (V) is more important. However, this ratio could be attributed to the inductive attraction between the substituents. The meta isomer would be stabilized more than the para if the inductive effect decreases with increasing distance. The meta/para ratio of 2.31 found for the diethylbenzenes is easily explained on the basis of the resonance structures (VI) and (VII). Both structures destabilize the para isomer relative to the meta.



(VI) (VII)

Disproportionation Constants.--Consider the disproportionation reaction of benzene containing labeled hydrogen as shown in reaction (3-3). Since hydrogen is defined as a substituent with zero polar effects (its

$$C_6H_5H^* + C_6H_5H^* \rightleftharpoons C_6H_6 + \underline{o}\text{-}, \underline{m}\text{-} \;\&\; \underline{p}\text{-}H^*C_6H_4H^* \qquad (3\text{-}3)$$

sigma values are defined as zero) the distribution observed should be completely random. A statistical treatment of the distribution yields values of 0.333 and 0.167 for K_d(meta) and K_d(para), respectively, or a value of 1.0 for both $3K_d$(meta) and $6K_d$(para). Also, using the equations (3-4) and (3-5) a value of 1.0 for both $3K_d$(meta) and $6K_d$(para) is calculated

$$\log 3K_d(\underline{\text{meta}}) = -\rho_{\underline{m}}\sigma_{\underline{m}\text{-}x}\sigma_{\underline{m}\text{-}y} \qquad (3\text{-}4)$$

$$\log 6K_d(\underline{\text{para}}) = -\rho_{\underline{p}}\sigma_{\underline{p}\text{-}x}\sigma_{\underline{p}\text{-}y} \qquad (3\text{-}5)$$

Groups with Hammett sigma constants of the same sign always give a positive multiplication product and thus by the equations (3-4) and

Table 26

Summary of Statistically Corrected Disproportionation Constants at 35.0°

Reaction	$3K_d$(meta)	$6K_d$(para)
PhBr-PhBr	0.111	0.113
PhBr-PhF	0.179	0.169
PhEt-PhEt	0.480	0.416
PhBr-$PhCH_3$	1.542	1.112
$PhCH_3$-$PhCH_3$	0.624	0.492
PhH*-PhH*	1.000	1.000

Table 27

Hammett Substituent Constants

Based on the Ionization of Benzoic Acids[a]

Substituent	σ_m	σ_p
Bromine	+0.391	+0.232
Fluorine	+0.337	+0.062
Methyl	-0.069	-0.170
Ethyl	-0.07	-0.151

[a]From the compilation of McDaniel and Brown (50).

50. D. H. McDaniel and H. C. Brown, J. Org. Chem., 23, 420 (1958).

Table 28

Tau Values (at 35°) Calculated Using Hammett Sigma Constants

Reaction	τ_m	τ_p	τ_m/τ_p
PhBr-PhBr	6.2 ± 0.1[a]	17.6 ± 0.1	0.35
PhBr-PhF	5.7 ± 0.1	53.7 ± 0.4	0.11
PhEt-PhEt	65.1 ± 0.6	16.7 ± 0.1	3.9
PhBr-$PhCH_3$	6.3 ± 0.2	1.2 ± 0.2	5.3
$PhCH_3$-$PhCH_3$[b]	48 ± 13	11.9 ± 1.1	4.0

Table 29

Sigma Values Calculated Assuming τ_m and τ_p Equal to 3.5

Reaction	Substituent	σ_m	σ_p
PhBr-PhBr	Bromo	+0.5223 ± 0.0018[c]	+0.5200 ± 0.0018
PhBr-PhF	Fluoro	+0.4092 ± 0.0038	+0.4240 ± 0.0040
PhEt-PhEt	Ethyl	-0.3017 ± 0.0014	-0.3300 ± 0.0008
PhBr-$PhCH_3$	Methyl	-0.1029 ± 0.0035	-0.0253 ± 0.0040
$PhCH_3$-$PhCH_3$	Methyl	-0.266 ± 0.024	-0.326 ± 0.031

[a]The average deviations were calculated using the average deviations of the disproportionation constants.

[b]The data were taken from Taylor, et al., (13).

[c]The average deviations were calculated from the deviations of the disproportionation constants and other sigma values where applicable.

(3-5) a disproportionation constant of less than the random value would always be calculated. However, if the two groups have sigma values opposite in sign, the disproportionation constants calculated would be larger than the random values. The statistically corrected disproportionation constants, tabulated in Table 26, are in qualitative agreement with the expected values. The bromobenzene-toluene reaction is the only one for which the substituents have Hammett sigma values of opposite signs and is the only reaction for which disproportionation constants larger than the random values were found.

Quantitative Tests.--The first quantitative test applied to the results was to determine whether a constant set of tau values existed using the Hammett sigma constants (listed in Table 27) derived from the ionization of benzoic acids and using the equations (3-4) and (3-5). The tau values, tabulated in Table 28, not only vary significantly in magnitude but also the τ_m/τ_p values vary more than forty-fold. This inconsistency shows that the Hammett sigma constants do not satisfactorily correlate the equilibrium data.

The next treatment was designed to determine whether there exists any set of sigma values which would correlate the data. Hine (6, 7) has found that τ_m and τ_p are both approximately equal to 3.0-3.5 in water at 25.0°. Haworth (50) has found that the value of tau has little dependence on the solvent. Therefore, a value of 3.5 will be assumed for τ_m and τ_p for all of the equilibrium solutions at 35.0°. Using

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50. H. W. Haworth, The Activity Coefficients of Certain Aromatic Compounds, Unpublished Ph. D. Thesis, Georgia Institute of Technology, 1962, p. 59.

the equations (3-4) and (3-5) the sigma values found for the bromine atom in the disproportionation of bromobenzene were used in calculating the sigma values for the fluorine and methyl substituents in the crossed reactions (Table 29). The sign of sigma was assumed positive for bromine and negative for ethyl and methyl substituents. Since experimental equilibrium disproportionation constants for toluene were not available from reference sources and were not obtained in the present work, it is necessary to use the data obtained for ethylbenzene as a substitute for the toluene data. This should be a valid approximation since the meta and para disproportionation constants are not influenced by steric effects but depend on the inductive and resonance effects of the substituents. The inductive effects of the two groups (methyl and ethyl) are essentially the same as shown by the Hammett meta sigma constants of -0.069 and -0.070 for methyl and ethyl respectively. The methyl group, however, is slightly more electron-donating than the ethyl from the para position; Hammett sigma values are -0.170 for methyl and -0.151 for ethyl. Thus the effect that causes a meta/para value of greater than 2.0 (2.3) for the diethylbenzenes is accentuated with the xylenes and a larger value would be expected. The increase in the meta/para ratio would probably occur by a lowering of the para disproportionation constant. The values for the disproportionation of toluene calculated (13) from thermodynamic data, K_d(meta) 0.20, K_d(para) 0.076 and meta/para 2.6, are in fair agreement with the values found for ethylbenzene, K_d(meta) 0.160, K_d(para) 0.069 and meta/para 2.3. A meta/para value of 2.9 was reported (15) for the xylene

isomerization equilibrium in toluene and a value of 2.4 reported (16) for the isomerization equilibrium of the ethyltoluenes.

The sigma values found for the bromine and ethyl substituents are qualitatively satisfactory. That is, the absolute values for the ethyl group are smaller than those found for the bromine atom. This agrees with the fact that ethyl is considered to be a less polar substituent than bromine. The sigma values calculated for the methyl group from the results of the bromobenzene-toluene reaction do not agree satisfactorily with those of the ethyl group. Furthermore, the calculated methyl meta sigma value is more negative than the para value. This does not agree with the results from the disproportionation of ethylbenzene or with the generally accepted theory that the methyl group has a greater electron-donor ability as a para substituent.

Some disproportionation constants calculated using various sigma values are shown in Table 30. Disproportionation constants for the bromobenzene-toluene reaction calculated using for the bromine substituent the sigma values found in the disproportionation of bromobenzene and for the methyl group the values found (for the ethyl group) in the disproportionation of ethylbenzene were at least twice the experimentally observed values and the meta/para ratio calculated was about 50 per cent low. Calculations using the methyl sigma values obtained from the bromobenzene-toluene reaction yield disproportionation constants for toluene that were about twice the values observed (for ethylbenzene). The calculated meta/para ratio was 1.85 whereas a ratio of 2.3 was found for the diethylbenzenes.

Table 30

Disproportionation Constants Calculated[a] Using Various Sigma Values

Reaction	K_d(meta)	K_d(para)	Meta/para
$PhBr-PhCH_3$[b]	1.187	0.665	1.78
$PhBr-PhCH_3$[c]	1.021	0.653	1.56
$PhCH_3-PhCH_3$[d]	0.306	0.166	1.85
$PhCH_3-PhCH_3$[e]	0.242	0.121	2.0
$PhBr-PhCH_3$[f]	0.773	0.387	2.0

[a] Using $\rho_m = \rho_p = 3.5$.

[b] Using $\sigma^{CH_3} = \sigma^{Et}$ and σ^{Br} = observed values, Table 29.

[c] Using σ^{CH_3} values from reaction 5, Table 29, and σ^{Br} = observed values.

[d] Using σ^{CH_3} values from reaction 4, Table 29.

[e] Using $\sigma_p^{CH_3} = \sigma_m^{CH_3} = -0.20$.

[f] Using $\sigma_p^{CH_3} = \sigma_m^{CH_3} = -0.20$ and σ^{Br} = observed values.

Calculations were carried out using a value of -0.20 for both the meta and para sigma values for the methyl group. The value -0.20 was an approximate average of the sigma values found in the ethylbenzene and bromobenzene-toluene reactions. The constants, shown in Table 30, calculated for the toluene disproportionation, K_d(meta) 0.24, K_d(para) 0.12 and meta/para 2.0, are not unreasonably different from those found (for ethylbenzene), K_d(meta) 0.160, K_d(para) 0.069 and meta/para 2.3. The constants calculated for the bromobenzene-toluene reaction, K_d(meta) 0.77 and K_d(para) 0.39, are not so different from the observed values, K_d(meta) 0.514 and K_d(para) 0.185, as to be unreasonable, especially since the use of control samples showed that the observed values may be low by as much as 10 per cent. However, the calculated meta/para ratio of 2.0 is difficult to reconcile with the experimental ratio of 2.775. In fact, no set of methyl sigma values is consistent with the bromine sigma constants in Table 29 and the meta/para ratios of greater than 2.0 found for the toluene (ethylbenzene) and the bromobenzene-toluene reactions.

The fluorine substituent, like methyl, is generally considered to have much greater electron-donor abilities from the para position; Hammett sigma constants (Table 27) are +0.337 and +0.062 for the meta and para fluorine substituents respectively. However, sigma values found in the bromobenzene-fluorobenzene reaction were +0.4092 and +0.4240 for the meta and para fluorine substituents respectively. This anomaly results from the experimental finding of a meta/para value of greater than 2.0. The bromine atom appears to destroy the resonance electron-donor ability of a group para to it.

The results of the bromobenzene-toluene reaction suggest that the inductive effect is the major factor in determining the isomer distribution. That is, the high ortho/para and meta/para ratios could be explained by an inductive attraction for which the effectiveness decreases with increasing distance. The groups in the bromobenzene-fluorobenzene reaction, however, repel each other by an inductive effect and thus the meta isomer should be destabilized relative to the para. However, the observed meta/para ratio of 2.1 shows that the meta isomer is favored. This meta/para ratio cannot be explained by resonance structures, either, as discussed previously.

CHAPTER IV

CONCLUSION

The data obtained in the present work on equilibrium reactions of the type

$$C_6H_5X + C_6H_5Y \rightleftharpoons C_6H_6 + XC_6H_4Y$$

cannot be correlated quantitatively using the Hammett equation or even a more general Hammett-type equation involving the dual-rho concept. Only qualitative agreement with equations previously derived to correlate data of the type obtained in this work was found.

CHAPTER V

RECOMMENDATIONS

In the disproportionation of bromobenzene the only tribromobenzene isomer detected was the 1,2,4 isomer. One might suspect that the 1,3,5 isomer would be present in larger amounts at equilibrium. It would be interesting to investigate the equilibrium. Hastings and Nicholson (52) reported the 1,2,4 isomer to predominate in equilibration of the trimethylbenzenes.

The disproportionation equilibrium of toluene could probably be reached in a reasonable length of time by starting with concentrations close to equilibrium value. Only about 5 per cent aluminum bromide should be used and sufficient amounts of hydrogen bromide bubbled into the solution. Good mixing of the hydrocarbon and catalyst phases appears to be necessary. Sealed tubes do not necessarily have to be used. A system such as that described by Schriesheim (12), using a reflux condenser to prevent loss of benzene, should prove useful.

The reaction of bromobenzene and ethylbenzene could be investigated to provide a check of the results of the bromobenzene-toluene reaction. Analysis would be complicated by formation of diethylbenzenes and dibromobenzenes but should be possible. The kinetically controlled products would probably be the diethylbenzenes but larger concentrations

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52. S. H. Hastings and D. E. Nicholson, J. Phys. Chem., 61, 730 (1957).

of bromoethylbenzenes should appear as the thermodynamically controlled products.

In the bromobenzene-toluene reaction the disproportionation constants were larger than random. If the constants tend to approach a more random distribution with increasing temperature, the disproportionation constants would decrease in value. The meta/para ratio would also decrease. It would be of interest to test this experimentally.

The reaction of ethylbenzene with chlorobenzene, fluorobenzene or toluene and the reaction of bromobenzene with chlorobenzene are possible. The importance of all such data, however, is questionable at the present time.

It is assumed that fluorobenzene would be even more inert than chlorobenzene to disproportionation. However, the type of substituent does not appear quite as important in intramolecular reactions and it would be of interest to see whether difluorobenzenes would undergo isomerizations under the same conditions used for the dichlorobenzenes.

APPENDIX

Calculation of ΔH° and Δs° for the Disproportionation of Bromobenzene.--
According to an integrated form of the van't Hoff equation (53)

$$\text{Log } K = \frac{\Delta H^\circ}{2.303RT} + \text{constant}$$

a plot of the logarithms of the equilibrium constants versus the reciprocal of the corresponding temperatures should yield a straight line.

Plots of log K versus 1/T, Figs. 2 and 3, were made from the data summarized in Table 31. Slopes of -254.4 and -194.1 were measured from

Table 31

Disproportionation Constants for Bromobenzene at 25.0°, 53.5° and 99.5°

Temperature, absolute	K_d(meta)	K_d(para)
298.0°	0.0400	0.0211
326.5°	0.0471	0.0249
372.5°	0.0556	0.0286

plots of the meta and para constants respectively. Using the equation

$$\text{slope} = -\Delta H^\circ/(2.303R)$$

values for ΔH° (meta) and ΔH° (para) were calculated. Using the general equation

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$$

53. S. Glasstone, Thermodynamics for Chemists, D. Van Nostrand Co., Inc., New York, N. Y., 1954, Chap. XIII.

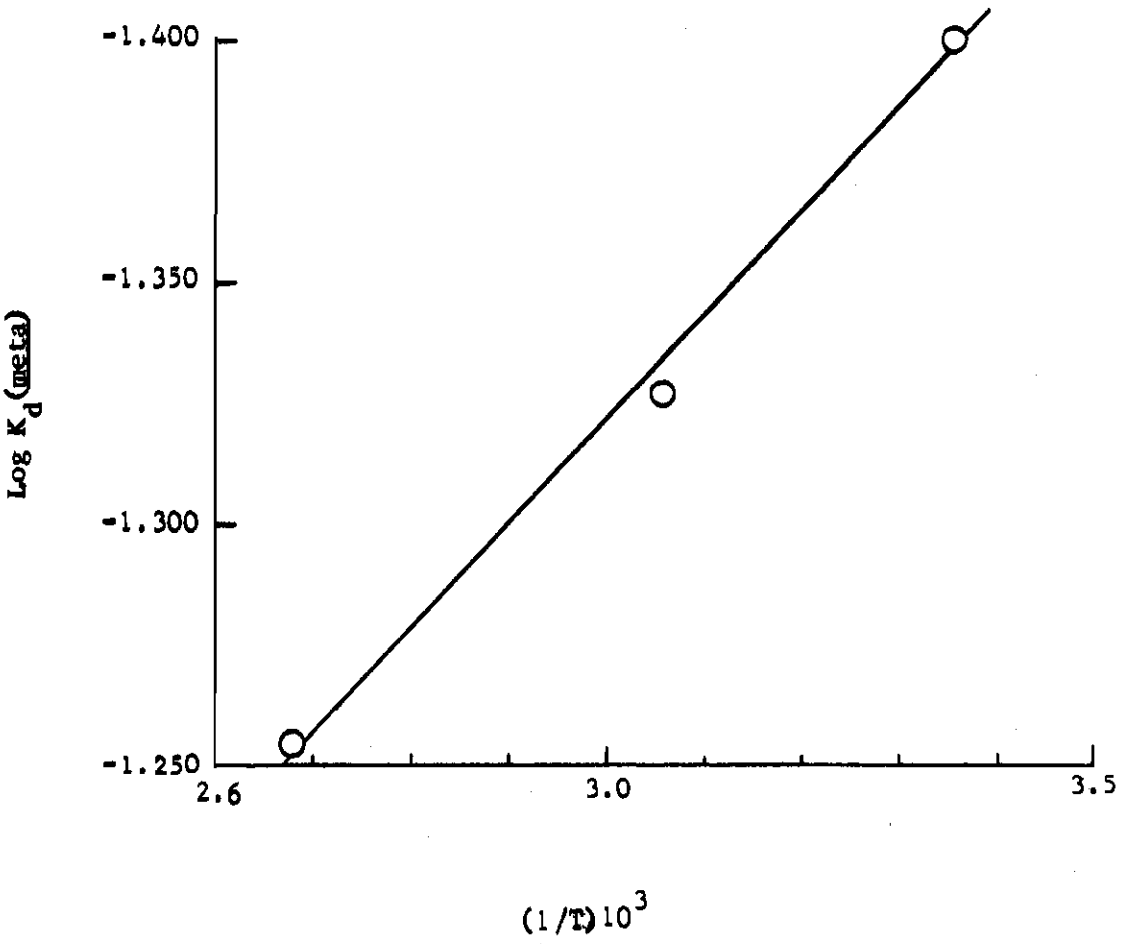

Fig. 2. Plot of Log K_d(meta) vs. $(1/T)10^3$ for the Disproportionation of Bromobenzene.

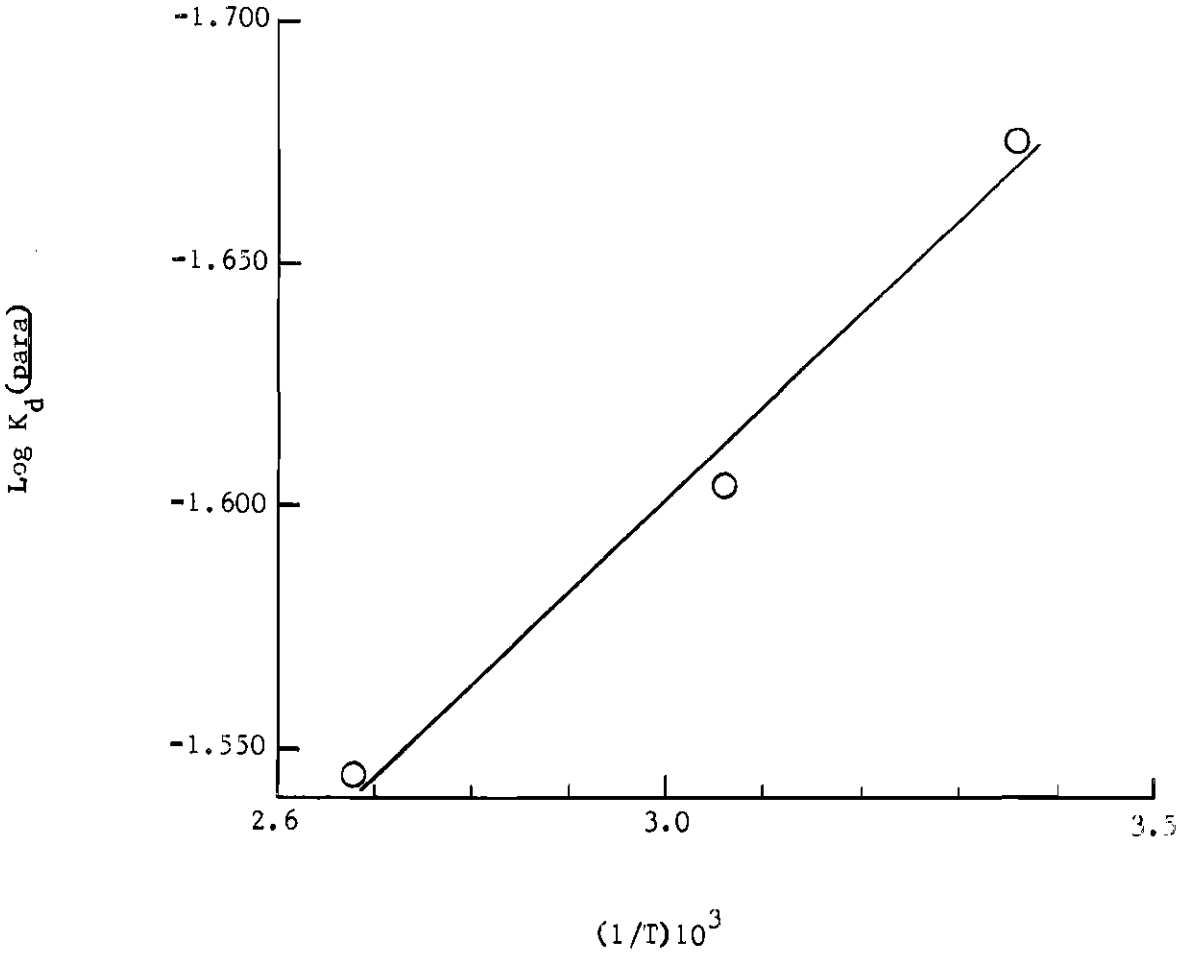

Fig. 3. Plot of Log K_d (para) vs. $(1/T)10^3$ for the Disproportionation of Bromobenzene.

and the relation

$$\Delta F^\circ = -2.303RT \log K$$

the equation

$$-2.303RT \log K = \Delta H^\circ - T\Delta S^\circ$$

is obtained. Corresponding values of log K and T were obtained from Figs. 2 and 3 and were substituted into the latter equation to yield values for ΔS°(meta) and ΔS°(para). The values are shown in Table 32.

Table 32

Calculated Values for ΔH° and ΔS° in Disproportionation of Bromobenzene

Equilibrium	ΔH° Cal/mole	ΔS° Cal/(deg)(mole)
$2C_6H_5Br \rightleftharpoons C_6H_6 + m\text{-}BrC_6H_4B_2$	960 ± 190	-3.2 ± 0.8
$2C_6H_5Br \rightleftharpoons C_6H_6 + p\text{-}BrC_6H_4Br$	890 ± 190	-4.7 ± 0.8

The average deviations were calculated assuming the average deviation of the equilibrium constants to be 5 per cent and assuming the average deviation are propagated according to equations given by Cook and Duncan (54).

The reason for the difference between the ΔS° values may be

54. G. B. Cook and J. F. Duncan, Modern Radiochemical Practice, The Clarendon Press, Oxford, England, 1952, p. 60.

investigated using the Boltzmann-Plank equation (55)

$$S = 2.303R \log W$$

where W is the probability of a particular state, thus

$$S_2 - S_1 = 2.303R \log (W_2/W_1)$$

Since the meta position is favored over the para by a factor of 2, the equation becomes

$$S_m - S_p = 2.303R \log 2 = 1.37$$

whereas a value of 1.5 (4.7 minus 3.2) was found. Thus within the experimental error the entropy difference between m- and p-dibromobenzene is due to the statistical contribution.

The data for the disproportionation at 35.0° were not included in the present calculations. Data for the reaction at 25.0°, 53.5° and 99.5° were obtained in one continuous operation of the chromatograph and these data are probably in error by an approximately constant factor. Thus the slope of the plot of log K versus 1/T is probably dependable although the intercept of the line is probably in error. If this is true $\Delta H°$ is a reliable value but the calculated magnitude of $\Delta S°$ is less negative than the true value.

Infrared Analysis for o-, m- and p-Bromotoluene.--The wave lengths (44) found suitable for the analysis were 13.404 microns for o-, 12.966 for m- and 12.445 for p-bromotoluene. Samples of each isomer were

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55. S. Glasstone, op. cit., p. 185.

weighed into 10 ml. volumetric flasks and diluted to the mark with isooctane. The absorbance of solvent versus the solvent and solution versus solvent were determined at each of the three wavelengths. The slit width openings used were 0.373, 0.419 and 0.487 microns at the wavelengths 12.445, 12.966 and 13.403 microns respectively. Since it was not possible to demonstrate that p-bromotoluene was not contaminated with the meta isomer and vice versa it was necessary to calculate two sets of extinction coefficients. On the basis of the assumption that the m- and p-bromotoluene were not contaminated with each other (1st assumption), the extinction coefficients shown in Table 33 were calculated.

Table 33

Molar Extinction Coefficients for the Bromotoluenes, 1st Assumption

Wavelength, microns	o-	m-	p-
12.445	7.0 ± 0.4	8.4 ± 0.3	298 ± 5
12.966	3.6 ± 0.5	235 ± 1	3.9 ± 1.6
13.403	360 ± 4	2.0 ± 0.7	0.5 ± 0.5

In the second assumption the m-bromotoluene was assumed to contain 2.3 per cent para and p-bromotoluene assumed to contain 2.1 per cent meta.[1] The extinction coefficients calculated are shown in Table 34.

[1] The reason for this is given in a following section of this Appendix.

Table 34

Molar Extinction Coefficients for the Bromotoluenes, 2nd Assumption

Wavelength microns	o-	m-	p-
12.445	7.0 ± 0.4	0.0	305 ± 3
12.966	3.6 ± 0.5	240 ± 3	0.0
13.403	360 ± 4	2.1 ± 0.7	0.5 ± 0.5

The samples for analysis collected from the preparative column O were dissolved in about one ml. of isooctane and the solution versus solvent and solvent versus solvent absorbancies determined as described above. The concentrations were then determined using the following equations for the first assumption

$$A^{(12.445)}/0.0185 = 7.0C_o + 8.4C_m + 298C_p$$

$$A^{(12.966)}/0.0185 = 3.6C_o + 235C_m + 3.9C_p$$

$$A^{(13.403)}/0.0185 = 360C_o + 2.0C_m + 0.5C_p$$

where A is the absorbance observed (at wavelength shown in parenthesis) for the solution, 0.0185 is the cell thickness and C_x is the concentration of the x-isomer.

The following set of equations were used to calculate the concentrations for the second assumption.

$$A^{(12.445)}/0.0185 = 7.0C_o + 0.0C_m + 305C_p$$

$$A^{(12.966)}/0.0185 = 3.6C_o + 240C_m + 0.0C_p$$

$$A^{(13.403)}/0.0185 = 360C_o + 2.1C_m + 0.5C_p$$

The calculations were carried out at the Rich Electronic Computer Center on a Burroughs 220. The computer programs were written by James B. Edwards, a chemical engineering graduate student.

Determination of Absolute Absorbancies.--In quantitative infrared analysis the difference between the solvent versus solvent and the solution versus solvent absorptions is taken as the absorbance of the substance in the solution. However, in the solution a certain amount of solvent has been displaced and the observed absorbance is lowered by an amount equal to the absorbance of the solvent displaced. The amount by which the absolute absorbance differs from the observed value will depend on how strongly the solvent absorbs at a given wavelength and on the concentration of the solution. If the solvent does not absorb an appreciable amount there will be no difference in the absorbancies.

The correction applied to infrared standard 7-7-2 will be used as an example. The concentration of m-bromotoluene (in isoöctane) was 1.568 moles/liter and its molar volume 0.12 liters/mole. Thus (1.568)(0.12) = 0.188 liter of isoöctane was displaced per liter of solution, assuming the volumes are additive. The molar volume of isoöctane is 0.165 liters/mole and thus the moles of isoöctane displaced, $\Delta C(iso.)$, is equal to 0.188/0.165 or 1.14.

The absorbance of isoöctane at each of the three wavelengths in question was determined at three cell thicknesses using a Perkin-Elmer variable space cell versus a clear reference path. The extinction coefficients were calculated using the equation $\epsilon(iso.) = \frac{(A_2 - A_1)}{(1_2 - 1_1)C}$

where C, the concentration of isoöctane, is 6.056 moles/liter. The extinction coefficients calculated for isoöctane were 0.251, 0.131 and 0.900 at 12.445, 12.966 and 13.404 microns respectively. The absorbance calculated for the isoöctane displaced, using the formula

$$A(iso.) = \epsilon(iso.) \cdot C(iso.) \cdot 0.0185$$

was added to the observed absorbance, A(obs.), to give the absolute absorbance A(abs.). The calculated quantities are given in Table 35.

Table 35

Absolute Absorbancies, A(abs.), Calculated for Infrared Standard 7-7-2

Wavelength microns	A(abs.)	A(iso.)	A(abs.)
12.445	0.250[a]	0.005	0.255
12.966	---	0.003	---
13.404	0.116	0.019	0.135

[a]The solution absorbed too strongly at 12.966 microns for accurate measurement.

Infrared Determination of the Impurity Limits of m- and p-Bromotoluene.--Several infrared standards were prepared using either m- or p-bromotoluene. Absolute extinction coefficients were determined by the method described in the preceeding section. Only absolute coefficients were used in the calculations.

First it was assumed that the absorption by m-bromotoluene at 12.445 microns was due to para isomer impurity. By this assumption the amount of m-bromotoluene actually put into a standard was less than

that weighed by the amount of *para* isomer estimated to be present. Thus a new extinction coefficient for *m*-bromotoluene at 12.966 microns had to be calculated. The absorption by *p*-bromotoluene at 12.966 microns was assumed to be due to *meta* isomer impurity. The concentration of the *meta* impurity present was calculated using the most recently determined *m*-bromotoluene extinction coefficient.

A new extinction coefficient for *p*-bromotoluene at 12.445 microns was calculated using the corrected *para* concentration. The process was repeated, each time using the most recent extinction coefficient, until a constant pair of extinction coefficients was obtained.

The following calculations are given to illustrate the method. The data are given in Table 36. For standard 7-5-2 the concentration

Table 36

Data on Two Infrared Standards for Impurity Limits Calculations

Standard	A(abs.) 12.445 microns	12.966 microns	Bromotoluene concentration moles/liter	Isomer used	Initial absolute extinction coefficent
7-5-2	0.011	0.316	0.07296	*meta*	234
7-5-3	0.267	0.006	0.04746	*para*	304

of the *para* isomer is given by

$$C_p = \frac{0.011}{(304)(0.0185)} = 0.00196 \text{ moles/liter}$$

The meta concentration is therefore

$$\begin{array}{r} 0.07296 \text{ moles/liter} \\ -0.00196 \quad " \quad " \\ \hline 0.07100 \quad " \quad " \end{array}$$

and the new extinction coeficient is

$$\epsilon_m^{(12.966)} = \frac{0.316}{(0.0716)(0.0185)} = 241$$

the concentration of the meta isomer in p-bromotoluene sample is

$$C_m = \frac{0.006}{(241)(0.0.185)} = 0.00135 \text{ moles/liter}$$

the new para concentration is

$$\begin{array}{r} 0.04746 \text{ moles/liter} \\ -0.00135 \quad " \quad " \\ \hline 0.04611 \quad " \quad " \end{array}$$

and the new extinction coefficient is

$$\epsilon_p^{(12.445)} = \frac{0.267}{(0.04611)(0.0185)} = 313$$

Recalculation of the para concentration in meta gives

$$C_p = \frac{0.011}{(313)(0.0185)} = 0.00190 \text{ moles/liter}$$

and

$$\epsilon_m^{(12.966)} = \frac{0.316}{(0.07106)(0.0185)} = 240$$

New calculations on the para standard give

$$C_m = \frac{(0.006)}{(240)(0.0185)} = 0.00135$$

$$\epsilon_p^{(12.445)} = \frac{(0.267)}{(0.04611)(0.0185)} = 313$$

Recalculation of the meta extinction coefficient gives a value of 240 and thus a constant set of coefficients has been reached. The impurity limits can therefore be calculated. The limit of the para isomer in m-bromotoluene is thus

$$\frac{0.00190}{0.07106} \times 100 = 2.7 \text{ per cent}$$

and the limit of the meta isomer in p-bromotoluene is

$$\frac{0.00135}{0.04611} \times 100 = 2.9 \text{ per cent}$$

These values were averaged with other determinations to give values of the impurity limits of 2.3 per cent meta isomer in p-bromotoluene and 2.1 per cent para in the m-bromotoluene.

Table 37

Disproportionation of Bromobenzene at 25.0°

Experiment	Time	K_d(meta)	K_d(para)	Meta/para
No. 1	16 days	0.0390	0.0204	1.91
No. 1	22 days	0.0410	0.0221	1.86
No. 1	22 days	0.0411	0.0214	1.92
No. 2	16 days	0.0447	0.0233	1.92
No. 2	22 days	0.0405	0.0216	1.87
No. 3	16 days	0.0457	0.0257	1.78
No. 3	22 days	0.0372	0.0197	1.88
No. 3	22 days	0.0374	0.0201	1.86
No. 4	1 day	0.082	0.148	0.55
No. 4	15 days	0.044	0.0235	1.87
No. 4	21 days	0.045	0.0244	1.86
No. 5	14 days	0.0366	0.0190	1.92
No. 5	20 days	0.0400	0.0209	1.91
No. 8	2 days	0.071	0.023	3.04
No. 8	6 days	0.0359	0.0183	1.96
No. 8	9 days	0.0353	0.0178	1.98
No. 8	14 days	0.0369	0.0185	1.99
No. 8	14 days	0.0358	0.0180	1.98

Table 38

Disproportionation of Bromobenzene at 53.5° and 99.5°[a]

Time, hrs.	Temp.	K_d(meta)	K_d(para)	Meta/para	Ortho/para
1	53.5°	0.0095	0.0221	0.43	0.15
24	"	0.0382	0.0237	1.61	0.17
48	"	0.0400	0.0230	1.73	0.16
72	"	0.0505	0.0268	1.88	0.14
72	"	0.0437	0.0229	1.91	0.15
1/4	99.5°	0.0102	0.0248	0.41	0.19
1	"	0.0362	0.0262	1.40	0.20
3	"	0.0550	0.0286	1.89	0.20
3	"	0.0531	0.0268	1.98	0.21
9	"	0.0587	0.0304	1.93	0.19

Av. equil. values

	K_d(meta)	K_d(para)	Meta/para
53.5°	0.0471 ± 0.0034	0.0249 ± 0.0020	1.90 ± 0.02
99.5°	0.0556 ± 0.0021	0.0286 ± 0.0012	1.93 ± 0.03

[a]Data from experiment No. 7.

Table 39

Disproportionation of Bromobenzene at 35.0°[a]

Sample	Benzene	Concentration, mole per cent Bromobenzene	Dibromobenzene m-	p-	o-
1 day[b]	16.25	67.28	10.35	5.31	0.82
2 days[b]	16.32	67.45	10.32	5.22	0.78
3 days[b]	16.18	67.39	10.40	5.27	0.78
4 days	16.29	67.22	10.40	5.28	0.81
Av.[c]	16.26 ± 0.16	67.36 ± 0.14	10.33 ± 0.12	5.26 ± 0.05	0.79
Control Sample (4-11-4)					
Found[b]	16.99 ± 0.09	66.06 ± 0.54	10.78 ± 0.36	5.37 ± 0.12	0.80
Prepd.	17.42	65.56	10.86	5.36	0.80
Control Sample (4-11-2)					
Found[b]	17.34 ± 0.36	66.90 ± 0.44	10.48 ± 0.04	5.32 ± 0.01	--
Prepd.	17.70	66.58	10.42	5.30	--

[a]Data from Experiment No. 10.

[b]Average of several determinations.

[c]Average of 18 determinations.

Table 40

. Benzene, Chlorobenzene and Dichlorobenzene

Concentrations in the Isomerization of p-Dichlorobenzene[a]

Time, hrs.	Temp.	Concentration, mole per cent				
		Benzene	Chloro-benzene	Dichlorobenzene o-	m-	p-
0			47			53
0.5	170°	0.2	46.5	0.1	0.5	53.0
3	170°	0.2	46.4	0.3	6.8	47.8
3	190°	0.68	43.4	1.0	21.4	33.6
8	190°	1.7	40.1	1.4	28.2	28.7

[a]Data from experiment No. 12.

Table 41

Disproportionation of Ethylbenzene at 35.0°

Sample	Concentration, mole per cent				
	Benzene	Ethylbenzene	Diethylbenzene		
			m-	p-	o-
Exp. No. 14					
3 days[a]	36.72 ± 0.31	48.28 ± 0.24	10.15 ± 0.11	4.40 ± 0.03	0.45
Exp. No. 15					
3 days[a]	38.47 ± 0.14	47.58 ± 0.01	9.37 ± 0.12	4.11 ± 0.04	0.48
Exp. No. 16					
6 days[a]	33.10 ± 0.06	49.39 ± 0.03	11.84 ± 0.04	5.12 ± 0.01	0.54
Control Sample (1-24-8)					
Found[a]	38.10 ± 0.67	45.47 ± 0.32	11.35 ± 0.22	5.07 ± 0.14	--
Prepd.	37.63	45.67	11.43	4.96	--
Control Sample (1-24-1)					
Found	36.86 ± 0.34	45.34 ± 0.20	11.75 ± 0.07	5.22 ± 0.04	0.86
Prepd.	37.42	45.09	11.55	5.13	0.81
Control Sample (1-24-2)					
Found	36.15 ± 0.06	45.79 ± 0.05	12.20 ± 0.06	5.32 ± 0.06	0.55
Prepd.	36.61	45.51	12.06	5.28	0.54

[a]Average of several determinations.

Table 42

Reaction of Bromobenzene with Fluorobenzene at 35.0°

Sample	Concentration, mole per cent					
	Benzene	Fluoro-benzene	Bromo-benzene	Bromofluorobenzene		
				m-	p-	o-
Exp. No. 19						
1 wk.[a]	13.36	44.95	31.83	6.37	2.97	0.53
Exp. No. 20						
1 wk.[a]	12.42	43.74	32.83	6.97	3.31	0.62
Exp. No. 21						
1 wk.[a]	11.75	43.48	33.38	7.25	3.50	0.64
Control Sample (3-22-5)						
Found[a]	14.13	43.09	32.73	6.36	3.00	0.70
Prepd.	14.07	43.00	32.84	6.36	3.03	0.70
Control Sample (3-22-1)						
Found[a]	12.77	43.45	32.88	7.04	3.23	0.64
Prepd.	12.72	43.64	32.77	7.00	3.22	0.65
Control Sample (3-15-1)						
Found[a]	11.40	39.57	38.78	6.36	3.21	0.69
Prepd.	11.50	39.20	38.93	6.40	3.25	0.72

[a]Average of several determinations. The average deviation was in no case larger than 1 per cent.

Table 43

Reaction of Bromobenzene with Toluene at 35°[a]

Experiment	Time, days	Concentration, mole per cent					
		Benzene	Toluene	Bromobenzene	Bromotoluene		
					o-	m-	p-
No. 22[a]	1	41.34	30.74	15.32	4.69	5.82	2.10
	4	38.51	29.06	17.64	5.53	6.85	2.41
No. 23[a]	1	37.53	28.70	18.20	5.82	7.19	2.57
	4	38.53	28.96	17.55	5.53	6.87	2.55
No. 24[a]	1	38.46	28.84	17.68	5.68	6.93	2.46
	4	38.94	28.86	17.76	5.50	6.55	2.40
No. 22[b]	1	41.45	30.82	15.36	4.70	5.71	1.96
	4	38.63	29.15	17.70	5.54	6.73	2.25
No. 23[b]	1	37.65	28.79	18.26	5.84	7.06	2.40
	4	38.65	29.06	17.61	5.52	6.75	2.30
No. 24[b]	1	38.58	28.93	17.69	5.69	6.80	2.30
	4	39.06	28.95	17.81	5.52	6.43	2.24

[a]Calculated using 1st-assumption extinction coefficients for bromotoluenes.

[b]Calculated using 2nd-assumption extinction coefficients for bromotoluenes.

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